

Attachment D
SWIFTRC UIC Inventory
Information Package

Geochemical Evaluation and Framework Development for the Sustainable Water Initiative for Tomorrow Proposed Managed Aquifer Recharge Program

Prepared for

United States Environmental Protection Agency

Revision Date December 2017



Contents

Section	Page
Acronyms and Abbreviations.....	v
1 Introduction	1-1
1.1 Initiative Framework.....	1-1
1.2 Report Purpose	1-2
1.3 Report Structure	1-2
1.4 About This Report	1-2
2 Geochemical Compatibility Issues.....	2-1
2.1 Background	2-1
2.2 Geochemical Compatibility Issues	2-1
3 Evaluation Approach	3-1
3.1 Recharge Water, Groundwater and Aquifer Matrix Media Characterization	3-1
3.1.1 Recharge Water Characterization.....	3-2
3.1.2 Groundwater Characterization	3-4
3.1.3 Aquifer Mineral and Clay Matrix Characterization	3-4
3.2 Evaluation Approach.....	3-5
3.2.1 Conventional Geochemical Analysis	3-5
3.2.2 Geochemical Modeling	3-6
4 Data Collection	4-1
4.1 Recharge Water Data.....	4-1
4.2 Groundwater Data	4-1
4.3 Aquifer Mineral and Clay Matrix Data	4-1
5 Evaluating Geochemical Compatibility	5-1
5.1 Data Observations	5-1
5.1.1 Recharge Water Data Observations and Discussion.....	5-1
5.1.2 Groundwater Data Observations and Discussion	5-7
5.1.3 Lithology Data Observations and Discussion.....	5-9
5.2 Mineral Dissolution/Precipitation Evaluation.....	5-18
5.2.1 Evaluation Results Mixing Between Recharge Water and Native Groundwater.....	5-18
5.2.2 Evaluation Results Recharge Water and Aquifer Matrix	5-23
5.2.3 Identification of Impacts Related to Dissolution and Precipitation.....	5-26
5.2.4 Mitigation Approaches for Mineral Dissolution and Precipitation Impacts	5-26
5.3 Clay Structure Fragmentation.....	5-30
5.3.1 Evaluation of Clay Structure Fragmentation Results	5-31
5.3.2 Identification of Impacts Related to Clay Structure Fragmentation.....	5-31
5.3.3 Mitigation Approaches for Clay Structure Fragmentation Impacts.....	5-31
5.4 Clay Particle Dispersion Evaluation.....	5-35
5.4.1 Influence of Ionic Strength	5-36
5.4.2 Candidate Mitigation Approaches for Clay Dispersion	5-40
6 Future Framework Implementation	6-1
6.1 Summary of Mitigation Approach	6-1
6.2 Selecting the Recharge	6-1

Section	Page
6.3	Aquifer Conditioning for Clays6-2
6.3.1	Pilot Testing an Aluminum Chloride Flush6-3
6.4	Next Steps6-3
7	References.....7-1

Tables

Table 1-1.	Summary Description of SWIFT Phases
Table 2-1.	Summary Geochemical Effects, Parameters and Issues
Table 3-1.	Summary Geochemical Characterization and Evaluation Approaches
Table 3-2.	Recommended Analysis for Samples collected During Pilot Testing
Table 4-1.	Summary of Field and Laboratory Water Quality Test Results
Table 5-1.	Criteria and Threshold Concentrations for Identifying Redox Processes in Groundwater
Table 5-2.	Results of Analysis with USGS Redox Program
Table 5-3.	Summary of Transmissivity from Packer Testing at TW-1
Table 5-4.	Summary of X-Ray Diffraction Results on Samples from TW-1
Table 5-5.	Average Interstitial Clay Content of PAS
Table 5-6.	Clay Mineralogy in Aquifer Sands and Confining Beds
Table 5-7.	Summary of Mineralogical Results
Table 5-8.	Identification of Impacts due to Mineral Dissolution and Precipitation
Table 5-9.	Summary of Modeling Results on Carbon-based Recharge Before and After Adding Calcium Chloride
Table 5-10.	Summary of Cation Exchange Capacity Found in Samples From TW-1
Table 6-1.	Summary of Mitigation Approach

Figures

Figure 4-1.	Site Map
Figure 4-2.	12-inch Diameter Single-Cased Test Injection Well
Figure 4-3.	Lithologic Log in PAS Nansemond TW-1
Figure 5-1.	Piper Diagram of Cation-Anion Chemistry of Recharge water and Native Groundwater from PAS
Figure 5-2.	Eh Line for Samples of Native Groundwater from Nansemond WWTP and Pilot Test Recharge Water
Figure 5-3.	Folk Classification of Sand Samples from TW-1 at Nansemond
Figure 5-4.	Clay Mineralogy in Aquifer Sand and Confining Bed Samples
Figure 5-5.	Dissolved Iron Concentrations with DO Reaction with Pyrite and Siderite
Figure 5-6.	pH in Presence of DO Reacting with Pyrite and Siderite
Figure 5-7.	Conceptual Depiction of Pyrite Oxidation
Figure 5-8.	PHREEPLOT Diagram Showing Arsenic and Iron Equilibrium
Figure 5-9.	Buffering of Reactions in the PAS with Carbon-based Recharge Water of Varying Alkalinity
Figure 5-10.	Mechanisms of Clay Particle Disaggregation and Migration During Injection Operations
Figure 5-11.	Relationship Between Clay Content and CEC
Figure 5-12.	Graph Showing Varying Ionic Strengths of Recharge and Native Groundwater
Figure 5-13.	Diagram of Diffuse Double Layer in Clay Minerals
Figure 5-14.	Effect of Changing Ionic Strength of Native Groundwater
Figure 5-15.	Stability Relationships among Minerals in the System CaO-Al ₂ O ₃ -SiO ₂ -H ₂ O at 25°C
Figure 5-16.	Stability Relationships among Minerals in the System Na ₂ O-Al ₂ O ₃ -SiO ₂ -H ₂ O at 25°C
Figure 5-17.	Effects of Di-/Trivalent Treatments on Clay Mineral Structure

Acronyms and Abbreviations

µg/L	microgram(s) per liter
As III	arsenite
As V	arsenate
ASR	aquifer storage and recovery
AWT	advanced water treatment
BAC	biologically activated carbon
BFI	bypass filter index
Ca	calcium
CaCl ₂	calcium chloride
CaCO ₃	calcium carbonate
CB	confining bed
CEC	cation exchange capacity
CRT	constant rate test
DO	dissolved oxygen
EDX	energy dispersive x-ray
fbg	feet below grade
Fe	iron
FeCO ₃	iron carbonate or siderite
FeS ₂	iron sulfide or pyrite
GSD	grain size distribution
HFO	hydrous ferric oxide
HRSD	Hampton Roads Sanitation District
ID	identification
K	potassium
kg/L	kilogram(s) per liter
LSI	Langlier Saturation Index
LPA	Lower Potomac Aquifer
MAR	managed aquifer recharge
MCL	maximum contaminant level
MDL	method detection limit
meq/100g	milli-equivalents per 100 grams
MFI	membrane filter index
Mg	magnesium

ACRONYMS AND ABBREVIATIONS

mg/L	milligram(s) per liter
mol/L	mole per liter
MPA	Middle Potomac Aquifer
mV	millivolt(s)
MW	monitoring well
Na	sodium
NA	not applicable
NaOH	sodium hydroxide
NM	not measured
NTU	nephelometric turbidity unit
ORP	oxidation-reduction potential
PAS	Potomac Aquifer System
pCi/L	picocurie(s) per liter
PMCL	Primary MCL
RO	reverse osmosis
SEM	scanning electron microscopy
SI	saturation index
SMCL	secondary MCL
SWIFT	Sustainable Water Initiative for Tomorrow
SWIFTRC	SWIFT Research Center
TDS	total dissolved solids
TOC	total organic carbon
TSS	total suspended solids
TW	test well
UIC	underground injection control
UPA	Upper Potomac Aquifer
USGS	United States Geological Survey
VADEQ	Virginia Department of Environmental Quality
WWTP	wastewater treatment plant
XRD	x-ray diffraction

Introduction

The Hampton Roads Sanitation District (HRSD) is undertaking a Sustainable Water Initiative for Tomorrow (SWIFT) by reusing highly purified wastewater as a resource for aquifer replenishment through advanced treatment and subsequent injection into the region's groundwater aquifers.

1.1 Initiative Framework

The project is currently arranged in a six-phased framework, where the conclusion of each phase is a juncture where HRSD can decide if and how to proceed to the next phase. This approach provides a screening process where potential initiation issues barriers are identified and addressed/mitigated if possible. The phases are as follows:

Table 1-1. Summary Description of SWIFT Phases

Initiative Phase	Phase Description
Phase 1 – Concept Feasibility	Evaluates overall feasibility concepts regarding treatability using AWT processes, potential membrane process concentrate treatability, aquifer recharge hydraulic injectability and recharge water/aquifer geochemical compatibility. Conceptual costs are estimated at an AACE International Class 5 level.
Phase 2 – Concept Development	Further refines and develops AWT and groundwater injection concepts and facility features/layouts. Pilot-scale process evaluations are conducted to assess and compare AWT concepts and in-situ performance.
Phase 3 – Concept Demonstration	Confirmation Testing is conducted on a demonstration scale (approximately 1 mgd flow rate). The facility operation is demonstrated through continuous operation of the AWT process and simultaneous injection of the treated water into the Potomac aquifer. Process and operational parameters will be evaluated and adjusted for subsequent design and operational criteria development.
Phase 4 – Facility Plan Development	Preliminary development facility layouts and implementation approaches are developed based on information obtained from the Phase 2 Pilot Plant and the Phase 3 Demonstration Facility. Further development of facility features, regulatory acceptance, public/stakeholder acceptance. Evaluation and development of financing and resources needs and schedule refinement.
Phase 5 – Implementation Plan Development	Define specific project packages and implementation schedule including delivery method(s), project packaging and sequencing. Final selection of plant sites and capacities for implementation and subsequent preparation of preliminary engineering documentation. Development of program management plan, regulatory approvals, and resource/capital improvement plan.
Phase 6 – Full-Scale Facility Implementation	Final facility design per selected delivery approach. Construction initiation, completion and operation of planned SWIFT facilities at each of the selected plant sites.

Note:

advanced water treatment = AWT

This phase of the project, Phase 4, focuses on the development of facility-specific information building on previous pilot-scale testing, process evaluations, water quality testing and preliminary planning.

This information will assist in confirming project direction through more detailed facility technical and cost information. The output from this phase is intended to inform an overall implementation plan that will guide full-scale implementation should the sustainable water initiative continue to prove beneficial to HRSD's mission.

1.2 Report Purpose

This document, Attachment D, is an attachment within the Underground Injection Control (UIC) Inventory Information Package ("UIC Inventory"). The purpose of this evaluation and framework development is to identify key geochemical issues related to the recharge of fresh water into aquifers containing brackish (native) groundwater and reactive minerals occupying the aquifer matrix and establishing measures to promote the long-term sustainability of the proposed managed aquifer recharge (MAR) initiative to protect potential water uses and the aquifer.

1.3 Report Structure

The report is divided into seven major sections:

Section 1 – Introduction: This section provides a project introduction, purpose and objectives, and overall report structure.

Section 2 – Geochemical Compatibility Issues This section presents background and issues related to geochemical compatibility of recharge water with groundwater and aquifer matrix mineralogy.

Section 3 – Evaluation Approach: This section describes alternative approaches for permitting concentrate discharges to surface waters.

Section 4 – Data Gathering Results: This section describes alternative approaches for permitting concentrate discharges to surface waters.

Section 5 – Evaluation Results: This section describes alternative approaches for permitting concentrate discharges to surface waters.

Section 6 – Development of a Geochemical Compatibility Framework: This section provides details on additional treatment for concentrate discharges and the potential benefits in terms of reduced pollutant loading to surface waters.

Section 7– Future Framework Implementation: This section presents concluding findings and assessment of technical feasibility of membrane concentrate management.

1.4 About This Report

This report is intended to form the foundation for the development of a more detailed and site-specific water quality management procedures for eventual full-scale implementation to achieve the stated objective. This report identifies key water quality and aquifer matrix geochemical issues and develops the basic framework for guiding future steps.

This evaluation uses site-specific information developed from in-situ water sampling at the Nansemond Treatment Plant site as well as treated water quality information developed from the operation of pilot-scale facilities treating secondary wastewater recharge water from the York River Treatment Plant.

The conclusions and recommendations in this report are based on the aforementioned information and evaluated according to industry-wide procedures and practices. The information is used to form basic guidelines that will be further refined and developed.

Geochemical Compatibility Issues

2.1 Background

A critical portion of SWIFT is the provision of recharge water to achieve safe, sustainable and affordable MAR of the Potomac Aquifer System (PAS). To accomplish a regional recharge program, characterization and evaluation of the physical and chemical viability of injecting highly purified water (recharge) into the PAS must be conducted. In recharging the PAS, the chemical compatibility, if not addressed correctly, can impose operational and environmental issues detrimental to the program. In addition to the geochemical relationships discussed in this report, physical issues (total suspended solids [TSS], temperature, pH, etc.) can cause clogging, potentially altering the operation of the demonstration MAR well.

This report addresses the chemistry of recharge water generated from a pilot testing system at HRSD's York River Wastewater Treatment Plant (WWTP), native groundwater, and aquifer minerals from the PAS beneath the Nansmond WWTP. These data are used in evaluating potential reactions between the recharge, native groundwater, and the aquifer mineralogy.

Once the chemical compatibility issues are characterized, they are addressed through mitigating measures comprising the pre-treatment of the recharge and/or the conditioning of the aquifer to stabilize (passivate) reactive clay and metal-bearing minerals in situ. This report describes the techniques applied in characterizing chemical compatibility between the recharge, native groundwater, and minerals residing in the matrices of the PAS. Mathematical modeling techniques, used in testing the viability of several pretreatment alternatives, are also discussed.

2.2 Geochemical Compatibility Issues

Geochemical compatibility issues relate to:

- Long-term well operability
- Regulatory Compliance
- Aquifer stability and preservation
- Potential water uses

The following table summarizes general geochemical compatibility issues, effects and categories of parameters for measurement and evaluation.

Table 2-1. Summary Geochemical Effects, Parameters and Issues

Potential Issue	Effect	Key Parameters	Media Interaction Evaluated
Mineral dissolution	Water quality impairment and aquifer matrix clogging	Metal bearing minerals, saturation index, Safe Drinking Water Act MCLs	Recharge Water/ Groundwater – Aquifer Matrix Recharge Water – Aquifer Matrix
Mineral precipitation	Aquifer matrix and well clogging	Metal bearing minerals, saturation index	Recharge Water/ Groundwater – Aquifer Matrix Recharge Water – Aquifer Matrix
Clay structure fragmentation	Well clogging, aquifer matrix clogging	Clay mineralogy, CEC of clays	Recharge Water – Aquifer Matrix

Table 2-1. Summary Geochemical Effects, Parameters and Issues

Potential Issue	Effect	Key Parameters	Media Interaction Evaluated
Filter pack disruption	Well pumps sand during backflushing	Sand content of pumped water	Not applicable.
Clay particle dispersion	Well clogging, aquifer matrix clogging	Ionic strength	Recharge Water – Aquifer Matrix
Physical clogging	Well clogging due to solids in recharge water	Solids loading	Recharge Water

Notes:

CEC = cation exchange capacity

MCL = maximum contaminant level

The following describes the geochemical compatibility issues in further detail:

- **Mineral Dissolution and mobilization**

Reactions between the recharge water and minerals in the aquifer matrices can dissolve minerals leaching their elemental components (Stuyfzand, 1993). Recharge water containing dissolved oxygen (DO) above anoxic concentrations or nitrate concentrations greater than laboratory method detection limits (MDLs) will react with common, reduced metal-bearing minerals like pyrite (FeS_2) and siderite (FeCO_3), to release iron and other metals like manganese that occupy sites in the mineral structure. Iron and manganese can precipitate as oxide and hydroxide minerals if they contact recharge water-containing DO and/or nitrate. Oxidation of arseniferous pyrite can release arsenic, creating a water quality concern in the migrating recharge water. Left unchecked leaching metals degrade the quality of water stored in the aquifer, violating Safe Drinking Water Act regulations, while limiting the use of the stored water by the local population.

Increasing the recharge water pH raises it above the solubility limit of iron, buffering the dissolution of iron-bearing minerals. Hydroxyl ions in sodium and potassium hydroxide will react with iron (Fe) II released from siderite or pyrite, oxidizing Fe II to Fe III. It precipitates hydrous ferric oxide (HFO) on the surface of these minerals, which then passivates the minerals to future reactions in the aquifer environment.

Following biotic or abiotic oxidation of Fe^{2+} to Fe^{3+} with DO, the Fe^{3+} readily precipitates. Assuming sufficient alkalinity is available, the Fe^{3+} precipitates as HFO on the surface of these minerals, which then passivates the minerals to future reactions in the aquifer environment. Increasing the recharge water pH raises it above the solubility limit of iron, buffering the dissolution of iron-bearing minerals.

- **Metals precipitation**

Metal-bearing minerals including oxides, hydroxides, sulfates, carbonates, and others can precipitate due to reactions between the recharge water and the native groundwater, or recharge water and aquifer mineralogy. These reactions most commonly occur when the recharge water contains DO at concentrations exceeding 1.0 to 2.0 milligrams per liter (mg/L), but can also occur if the pH of the recharge water exceeds 9.0. As surface areas in the aquifer increase geometrically away from the well, mineral precipitation does not create as great a concern as the same reactions at the borehole wall. Considering the relatively small surface areas around the wellbore, precipitating metal-bearing minerals can clog pore spaces, and reduce permeability and well injectivity.

- ***Ionic Strength and Mineral Cationic Exchange Capacity Potential between recharge and groundwater***

Recharging recharge water exhibiting a significantly lower ionic strength than the native groundwater can damage interstitial clay minerals attached to aquifer framework particles, weaken inter-particle attachments, and even weaken charges in individual clay layers. Damage can also arise when recharge water displays differing cation chemistry than the native groundwater and the clay minerals (Langmuir, 1997). Exchanging cations can disrupt the clay mineral structure particularly when their atomic radius exceeds the radius of the exchanged cation. The larger cation fragments the tabular structure, shearing off the edges of the mineral. All these factors cause clay minerals and mineral fragments to migrate through the pore spaces of the aquifer. The fragments eventually block pore throats, reducing the permeability of the aquifer around a recharge well, diminishing the well's injection capacity.

- ***Solids loading in recharge water***

Recharge water can contain small amounts of TSS. If left to accumulate in the borehole environment (wellbore), solids can clog the screen, filter pack, and aquifer proximal to the well, which reduces the well's injectivity. Injectivity reduction increases draw-up and eventually lowers the well's injection capacity (Pyne, 2005). TSS can originate from scale or dirt in piping and treatment residuals.

Once the physical and chemical compatibility issues are characterized, they are addressed through selected engineering measures comprising the pre-treatment of the recharge water and/or the conditioning of the aquifer to stabilize (passivate) reactive clay and metal-bearing minerals in situ.

The techniques applied in characterizing physical and chemical compatibility between the recharge water, native groundwater and minerals residing in the matrices of the PAS are described in subsequent sections below.

Evaluation Approach

This section presents and discusses the approach to evaluating the characteristics of the recharge water, groundwater and aquifer matrix mineralogy and impacts/issues arising from their interaction in the recharge of treated water into the PAS. The table below identified the media where the potential issue exists.

Table 3-1. Summary Geochemical Characterization and Evaluation Approaches

Potential Issue	Media to be Characterized	Evaluation Approaches
Mineral dissolution	Recharge Water/ Groundwater – Aquifer Matrix Recharge Water – Aquifer Matrix	Geochemical modeling of interactions between native groundwater (test well), recharge water (from pilot plants), aquifer matrix (test well)
Mineral precipitation	Recharge Water/ Groundwater – Aquifer Matrix Recharge Water – Aquifer Matrix	Geochemical modeling of interactions between native groundwater (test well), recharge water (from pilot plants), aquifer matrix (test well)
Clay structure fragmentation	Recharge Water – Aquifer Matrix	Classify major cations of the native groundwater (test well), recharge water (from pilot plants), /compare aquifer matrix CEC (test well)
Clay particle dispersion	Recharge Water – Aquifer Matrix	Geochemical modeling of interactions between native groundwater (test well), recharge water (from pilot plants), aquifer matrix (test well)
Physical clogging	Recharge Water	Filtration techniques on recharge water

Based on the above, the following media must be characterized for thorough understanding and further evaluation:

- Recharge Water
- Groundwater
- Aquifer Matrix Mineralogy

The data derived from characterizing the different media are used in the evaluation of the following interactions between the media:

- Recharge Water/ Groundwater (Mixing) to Aquifer Matrix
- Recharge Water to Aquifer Matrix

The following approach is used to evaluate these interactions:

- Conventional Geochemical Analysis
- Geochemical Modeling

3.1 Recharge Water, Groundwater and Aquifer Matrix Media Characterization

The following media will be characterized:

- Recharge Water
- Groundwater

- Aquifer Mineral and Clay Matrix

3.1.1 Recharge Water Characterization

3.1.1.1 Physical Characterization Approach

Two testing techniques are used to quantify the solids content of recharge water. These techniques comprise membrane filter index (MFI) which estimates instantaneous (short-term) clogging rates, while bypass filter index (BFI) testing provides indices for long-term clogging rates. MFI testing uses a portable device that an operator can attach to various points along a run of pipe, or at the wellhead, whereas, the BFI device is permanently attached to the wellheader piping.

Similar to the MFI testing, BFI employs a filter device to measure the bypass filter index, TSS concentrations, and ultimately clogging indices in the recharge water. Where an operator, or other personnel can run an MFI test in 30 to 45 minutes, BFI tests require several weeks for the flowrate through the device to decline to 20 percent of its original rate.

These tests evaluate physical characteristics of the recharge water for injection compatibility. These techniques are employed **after** construction of the Demonstration Plant because they relate directly to the quality of recharge water exiting the plant.

3.1.1.2 Chemical Characterization Approach

To assess the chemical compatibility of a recharge water, water quality samples must be collected that are representative of the specific recharge water. These data are typically obtained from pilot testing facilities such as HRSD's pilot system at the York River WWTP. Several samples are collected from the selected treatment process to define the range of chemistry. Samples are analyzed for a comprehensive set of field and laboratory analytes that define the recharge water chemistry (Table 3-2).

Table 3-2. Recommended Analysis for Samples collected During Pilot Testing

Constituent	Units	MDL
pH	standard units	NA
Eh (corrected)	mv	50
Specific Conductivity	emhos	10
Dissolved Oxygen	mg/L	0.01
Temperature	°C	NA
Turbidity	NTU	0.1
Field Sulfate	mg/L	5
Field Iron (ferrous)	mg/L	0.01
Field Iron (total)	mg/L	0.01
Field Manganese	mg/L	0.01
Arsenic	mg/L	0.001
Chloride	mg/L	1
Field CO ₂	mg/L	1
Aluminum dissolved	mg/L	0.01
Aluminum total	mg/L	0.01

Table 3-2. Recommended Analysis for Samples collected During Pilot Testing

Constituent	Units	MDL
Arsenic dissolved	µg/L	0.001
Arsenic total	µg/L	0.001
Iron dissolved	mg/L	0.01
Iron total	mg/L	0.01
Manganese dissolved	mg/L	0.005
Manganese total	mg/L	0.005
Magnesium total	mg/L	1
Potassium total	mg/L	1
Sodium total	mg/L	1
Calcium total	mg/L	1
Sulfate	mg/L	1
Sulfide	mg/L	0.01
Alkalinity	mg/L	1
Nitrate as N	mg/L	0.01
Total Kjeldahl Nitrogen	mg/L	0.1
Fluoride	mg/L	0.01
Silica	mg/L	1
Total organic carbon	mg/L	0.5
Total phosphorus	mg/L	0.1
Ortho-phosphate	mg/L	0.01
Total dissolved solids	mg/L	10
Total suspended solids	mg/L	1
Hardness	mg/L	10
Ammonia	mg/L	0.1
Total trihalomethanes (THMs)	µg/L	1
Chloroform	µg/L	1
Bromoform	µg/L	1
Bromodichloromethane	µg/L	1
Dibromochloromethane	µg/L	1
Total haloacetic acids (HAAs)	µg/L	0.1

Notes:

µg/L = microgram(s) per liter

MDL = Method Detection Limit

NTU = nephelometric turbidity unit

3.1.2 Groundwater Characterization

The chemical characterization of the groundwater is important in the evaluation of the overall compatibility of recharge water relative to both the native groundwater and the aquifer mineral content. Collecting field data to assess the chemical compatibility of a native groundwater involves obtaining samples representing the water quality from each aquifer that will receive recharge water.

At the Nansemond test well, water quality samples were collected during packer testing conducted in isolated, screen intervals installed against the Upper Potomac Aquifer (UPA), Middle Potomac Aquifer (MPA), and Lower Potomac Aquifer (LPA). The three samples represent the native groundwater from each aquifer. In addition, a sample was collected while pump testing the test well.

Similar to the recharge water, native groundwater samples are analyzed for a comprehensive set of field and laboratory analytes (Table 3-2).

3.1.3 Aquifer Mineral and Clay Matrix Characterization

During drilling of the test wells, drill cuttings were collected at 10 foot intervals through the total depth of the wellboring and used to characterize the lithology with particular attention to the grain size, color of the sediments, sorting, and mineralogy. In addition to the boring log, the geologist prepares a graphic log of the wellboring that shows the thickness of aquifer units, confining beds, salient grain size, and distribution of minerals. Contacts on the graphic log are coordinated with the geophysical log, which is run upon reaching the total depth of the borehole. Results from the mineralogical lab's analysis of the samples are added to the graphic log, upon their release.

3.1.3.1 Mineralogical Laboratory Analysis

Following the logging of cuttings, intervals are selected for mineralogical analysis by a specialty laboratory. Samples of the aquifer and confining unit matrices are selected for mineralogical analysis by a specialty laboratory. The samples are analyzed for bulk and clay fraction x-ray diffraction (XRD) and energy dispersive x-ray (EDX) analysis to determine their mineralogical and elemental composition, respectively. Then samples undergo supporting analyses according to their composition and hydrologic significance (aquifer sands, confining bed clay, intra aquifer clay, etc.).

In addition to XRD and EDX, aquifer materials consisting of sand undergo the following analyses:

- Quantitative thin section petrography (300-point count, and pore-filling composition)
- Laser particle size analysis
- Specific gravity

Samples originating from confining units are analyzed for the following (plus XRD and EDX):

- Qualitative thin section petrography
- Scanning electron microscopy (SEM)
- Core description
- CEC

Attempts at CEC analysis in aquifer sands failed because of lack of sample material

3.1.3.2 Aquifer Mineral and Clay Matrix Characterization Evaluation

Evaluating aquifer samples includes the following steps:

- Characterizing aquifer sand types using the Folk classification system
- Identifying reactive minerals in the aquifer and confining units
- Plotting the mineralogy on the graphic log of the test well

- Normalizing the clay mineralogy for aquifer sands and confining beds
- Applying the CEC to represent interstitial clay suites in aquifer sands.

Because disrupting clays in the PAS can profoundly influence injection operations, the last two items hold the greatest significance for formation samples from HRSD's test well sites. The clay mineralogy and CEC results will help constrain the input and interpretation of geochemical modeling results.

Clay mineral suites were normalized to 100 percent in the aquifer and confining bed samples and then the mineral suites were evaluated for their distribution through the section. At the Nansemond site, the clay mineral suite in the Potomac Confining bed above the UPA exhibited a significantly differing mineral distribution, independent of the suite displayed in the interstitial clays in the UPA, MPA, and LPA and their intervening confining beds.

To estimate a CEC for interstitial clays occupying the pore spaces of aquifer sands, CECs in the confining beds were projected onto adjacent sands proportionally reducing CEC values based on the clay content in the sands. Although cation exchange does not present a great concern for recharge operations, it is anticipated to be useful for potential aquifer conditioning activities to help strengthen and stabilize clay minerals.

3.2 Evaluation Approach

3.2.1 Conventional Geochemical Analysis

The following items will be evaluated using statistical, graphing, and plotting techniques on the recharge water and native groundwater chemistry:

- Determine and describe predominating ionic species and the relationship between samples
 - Piper Diagrams
 - Stiff Diagrams
- Determine and describe the redox conditions of the recharge water and mixed water to evaluate the mobility of metals in the aquifer and changing redox conditions caused by a recharge water containing DO reacting with aquifer minerals
 - Redox diagram
 - Redox Constituent Analysis
- Assess the stability of clays and metal-bearing minerals (iron, manganese, aluminum, arsenic, etc.) in the aquifer matrix
 - Parametric statistics
 - Correlation Coefficients
 - Regression Analysis
 - Phase Diagrams

Piper and Stiff diagrams plot cation and anion percentages on triangular and polygonal grids, respectively, to graphically display the predominating ionic species and the relationship between samples. Spreadsheet and customized computer programs (HC-Gram - U.S. Department of Interior, 2005) are available to develop Piper and Stiff diagrams. Several programs also plot total dissolved solids (TDS) or ionic strength data with the prevailing ions.

Redox line diagrams and the Jurgens et. al (2009) redox constituent analysis help describe redox conditions of the recharge water or storage aquifer based on aqueous analysis. These techniques become particularly important when considering the mobility of metals in the aquifer or changing redox conditions caused by a recharge water containing DO reacting with aquifer minerals. Under the circum-

neutral pH conditions, typical at most recharge facilities, redox conditions control the mobility of arsenic and the adsorption characteristics of aquifer minerals that can hinder arsenic mobility.

Phase diagrams will be developed to assess the stability of clays and metal-bearing minerals (iron, manganese, aluminum, arsenic, etc.) in the aquifer matrix. The program PHREEPLOT (Kinniburgh, 2011) was used in preparing predominance-area, log-activity, log-concentration, and other types of phase diagrams. The geochemical equilibrium model, PHREEQC (Parkhurst, 1998), developed by the United States Geological Survey (USGS) supports developing the phase diagrams for clays by calculating the activity of constituents making up common clay minerals.

3.2.2 Geochemical Modeling

Geochemical modeling is used to:

- Simulate reactions between recharge water, native groundwater, and aquifer mineralogy
- Simulate treatment (aquifer conditioning) techniques to stabilize minerals or complexes in situ
- Predict the long-term changes in the chemical environment of the accepting aquifer

The geochemical modeling involves the following:

- Speciating ions and complexes
- Developing saturation indices (SIs) for potential mineral phases
- Calculating ionic strengths of aqueous samples
- Calculating activities of constituents for plotting phase diagrams

3.2.2.1 Modeling Software Summary Description

PHREEQC, PHREEPLOT, and MINTEQA2 (Allison, 1991) are used in performing the geochemical modeling simulations. PHREEQC performs a number of useful functions for evaluating the data from HRSD test sites including transport, mixing, cation-exchange, surface complexation, simple chemical reactions, speciation, and inverse modeling.

MINTEQA2 was developed by the United States Environmental Protection Agency to perform equilibrium calculations on metals contaminating groundwater at Resource Conservation and Recovery Act and Comprehensive Environmental Response, Compensation, and Liability Act sites. The program does not display the extensive capabilities of PHREEQC, but employs several functions that will prove useful for evaluating data from the HRSD test sites, including a cation exchange module, and a wide range of surface complexation (Langmuir, Freundlich, Diffuse Double-Layer, Triple Layer and Constance Capacitance) models.

3.2.2.2 Modeling Approach

The modeling will be accomplished utilizing a three-phased approach:

Phase 1 geochemical modeling – Evaluation of Recharge and Groundwater

The first modeling simulations were run by using the analytical results from recharge water and native groundwater samples as input. Modeling was also conducted with native groundwater and aquifer minerals to help decipher minerals controlling the solubility of metals, and ligands dissolved in water. Modeling involved reacting minerals identified in the aquifer samples with constituents in the recharge water like DO, nitrate, dissolved iron and others. The simulations help characterize the mobility of common trace metals in the aquifer environment after injection. By identifying these metals through modeling, the analyst can test the effectiveness of pretreatment schemes in stabilizing metals in situ.

Phase 2 geochemical modeling – mitigating metals mobilization

The process involves adding agents to the recharge water to precipitate minerals containing the trace metal. Surface complexation functions are also employed in assessing the adsorption capacity of metal

oxide surfaces developed from precipitating minerals composed of trace metals. Adsorption often exhibits greater effectiveness in stabilizing trace metals or reactive metal bearing minerals in situ than precipitation reactions. The following sequence describes the stepped approach to the second phase of modeling:

- Reactive constituents in recharge water with native groundwater (mixing) and aquifer minerals
- Test pretreatment schemes to stabilize dissolved trace metals and reactive metal bearing minerals.
- Assess the capacity of metal oxide minerals to adsorb trace metals in aquifer environment

Phase 3 geochemical modeling - clay stability enhancement

The third phase of modeling involves stability of clay minerals and represents an important aspect of the geochemical modeling for evaluating data from the HRSD test sites. Geochemical modeling can help establish the stability of clay minerals in the native aquifer environment and after recharge, but they add little to evaluating how the changing charge strength between native groundwater and recharge water affects the stability of interstitial clays. This critical portion of the evaluation has to rely on studies performed at other recharge sites. The following sequence describes the approach for testing ion exchange conditioning schemes to assess which produces the greatest clay stability:

- Determining the native geochemical clay stability
- Evaluating clay mineral stability after injection
- Apply clay mineral suites and CEC from aquifer lab analysis
- Evaluating conditioning schemes with divalent ions, testing various cations and dosages.
- Evaluating conditioning schemes with trivalent ions
- Testing the addition of divalent ions to recharge water to maintain stability created by conditioning

A characteristic of modeling common to all projects involves questions arising that require further modeling and testing. Thus, the modeling approach can change while conducting a project, often focusing the effort toward better solutions, while dictating modifications on the modeling approach to future projects.

Data Collection

Properly evaluating the compatibility between recharge, native groundwater, and aquifer mineralogy required obtaining samples of the plant recharge water, native groundwater from each aquifer unit screened by the MAR well, and formation samples from the PAS. Recharge samples were obtained from the pilot testing plant located at the York River WWTP where HRSD personnel tested membrane-based and carbon-based treatment processes. To obtain native groundwater and formation samples from the PAS, HRSD installed, developed, and tested a MAR test well (TW-1) at their Nansemond WWTP between April and September 2016 (Figure 4-1). The well boring was drilled to 1,410 feet below grade (fbg), fully penetrating UPA and MPA, and penetrating through the upper portion of the LPA. With the exception of several thinner sand intervals that were not screened, screens in TW-1 fully penetrated the UPA and MPA, and the upper portion of the LPA from 1,210 to 1,410 fbg (Figure 4-2).

Following development, TW-1 underwent a step drawdown test, a 24-hour constant rate aquifer test, and packer testing in the UPA, MPA, and LPA. Water quality samples were collected at the end of the constant rate test and the packer testing of the individual PAS aquifers (Table 4-1).

4.1 Recharge Water Data

As noted in Section 3-1 of this report, water quality samples were collected and analyzed from the pilot plant operation (Table 4-1)

4.2 Groundwater Data

At TW-1, three groundwater samples were collected during packer testing conducted in isolated screen intervals installed against the UPA, MPA, and LPA. These three samples represented the native groundwater from each aquifer. In addition, a sample was collected at the end of the 24-hour pumping period of the constant rate test. The sample represented a mixture of native groundwater from the three aquifers, providing a useful check on the bulk chemistry from each aquifer, but does not substitute for the packer testing samples. Similar to the recharge samples, the native groundwater samples were analyzed for a comprehensive set of field and laboratory analytes (Table 4-1).

4.3 Aquifer Mineral and Clay Matrix Data

During drilling of test well TW-1, the drilling crew collected cuttings at 10 foot intervals through the total depth of the well boring. In addition to CH2M, personnel from the Virginia Department of Environmental Quality (VADEQ) oversaw the drilling and collection of samples. VADEQ employed several visual tracers to map the travel time of cuttings from the drilling bit to the ground surface. They worked closely with the drilling subcontractor to ensure samples collected at the ground surface accurately reflected the depth of drilling.

The samples were cleaned, with an aliquot spread across a paper sheet covering the ground surface and the remainder stored in 1 quart jars. A CH2M geologist logged the lithology of the cuttings with particular attention to the grain size, color of the sediments, sorting, and mineralogy.

In addition to the boring log, the geologist prepared a graphic log of the well boring showing the thickness of aquifer units, confining beds, salient grain size, and distribution of minerals (Figure 4-3). Contacts on the graphic log were coordinated with the geophysical log, which was run upon reaching the total depth of the borehole. Results from the mineralogical lab's analysis of the samples were added to the graphic log, upon their release.

Following the logging of cuttings, intervals were selected for mineralogical analysis by Mineralogy, Inc., a laboratory specializing in mineralogical and petrophysical analysis located in Tulsa, Oklahoma.

The laboratory analyzed all samples for bulk and clay fraction by XRD and EDX analysis in determining their mineralogical and elemental composition, respectively. Then samples underwent supporting analyses according to their composition and hydrologic significance (aquifer, confining bed, intra aquifer clay, etc.).

In addition to XRD and EDX, aquifer sands underwent the following analyses:

- Quantitative thin section petrography (300-point count, and pore- filling composition)
- Laser particle size analysis
- Specific gravity

Samples originating from confining units were analyzed for the following (plus XRD and EDX):

- Qualitative thin section petrography
- SEM
- Core description
- CEC



Figure 4-1. Site Map

Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

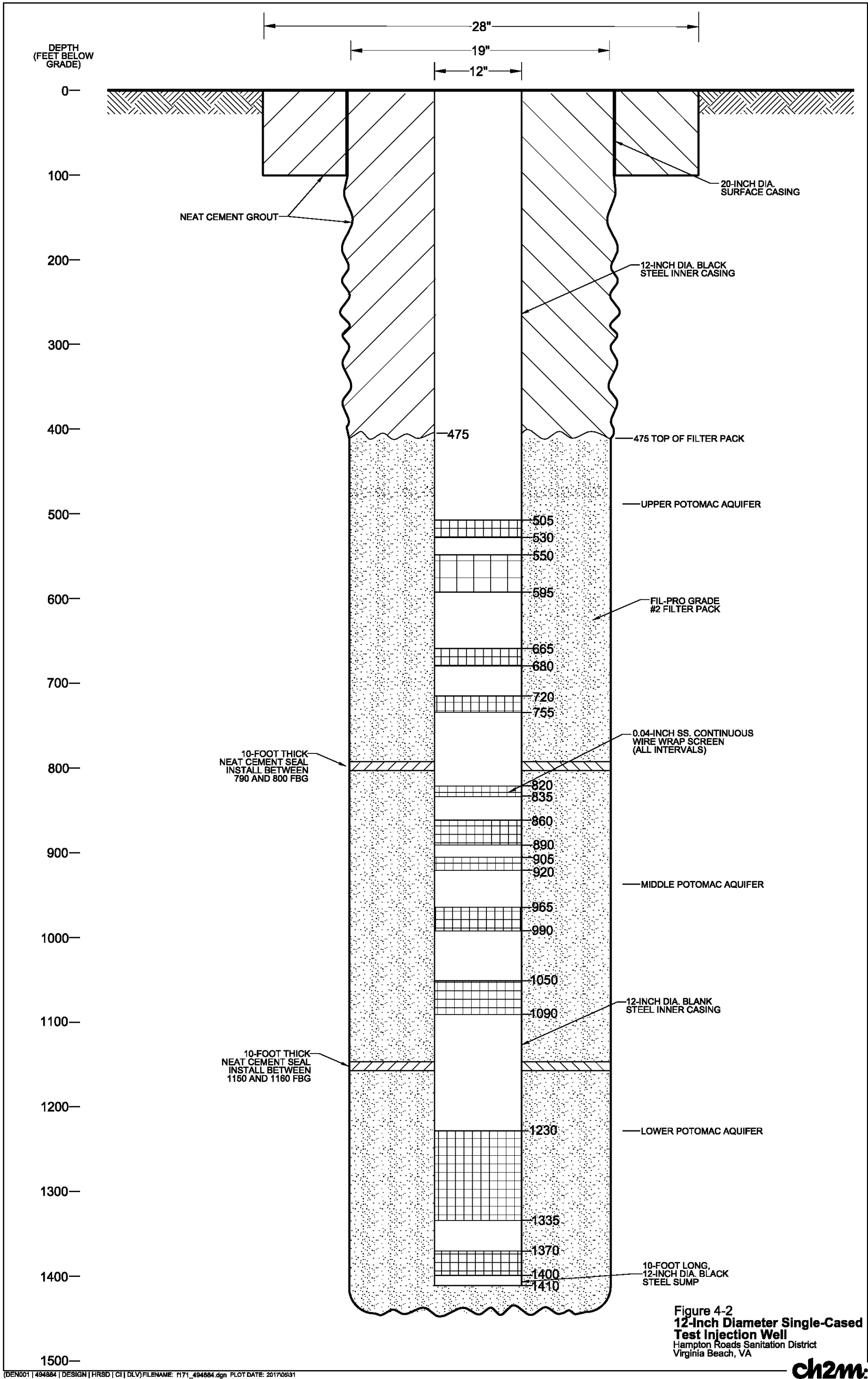


Figure 4-2. 12-inch Diameter Single-Cased Test Injection Well
Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads
Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

Table 4-1. Summary of Field and Laboratory Water Quality Test Results

Data Collection Results

Sample ID Test Info Constituent	Units	SWR_NPW1 24 Hr CRT 8/4/2016	SWR-NP012 Packer Test #1 (bottom zone) 8/11/2016	SWR-NP023 Packer Test #2 (middle zone) 8/17/16	SWR-NP034 Packer Test #3 (upper zone) 8/23/16	BAC Pilot Eff. Pilot test at York River5 8/5/16	RO Pilot test at York River6 8/5/16	Primary & Secondary MCL7
pH	standard units	7.71	7.19	7.21	7.13	6.96	6.00	6.5 - 8.5
Eh (corrected)	mv	97	50	66.5	57.6	471	725	
Specific Conductivity	emhos/cm	2.278	6.732	6.203	8.574	0.729	0.029	
Dissolved Oxygen	mg/L	0.15	0.23	0.74	0.2	17.5	5.1	
Temperature	°C	23.8	27.8	28.15	27.8	28.4	28.8	
Turbidity	NTU	1.31	1.67	0.68	0.46	NM	NM	
Field Chloride	mg/L	453	1906	1755	2257	NM	NM	
Field Carbon Dioxide as CaCO ₃	mg/L	23	35-40	35-40	40	21.8	5.4	
Field Total Sulfide	mg/L	0.02	0	0	0.01	<0.1	<0.01	
Field Sulfate	mg/L	37	140-200	104	248	NM	NM	250
Field Iron (ferrous)	mg/L	0.12	2.43	2.42	3.17	NM	0.01	0.3
Field Iron (total)	mg/L	0.2	3.18	2.75	4	NM	0.01	0.3
Field Alkalinity as CaCO ₃	mg/L	480	>400	360	340	110	210	
Aluminum dissolved	mg/L	<0.040	<0.04	<0.04	<0.04	<0.04	<0.04	0.2
Aluminum total	mg/L	<0.040	<0.04	<0.04	<0.04	<0.04	<0.04	0.2
Arsenic dissolved	mg/L	0.0003	0.0007	0.001	0.0005	NM	NM	0.01
Arsenic total	mg/L	0.0003	0.0006	0.00053	0.0005	NM	NM	0.01
Iron dissolved	mg/L	0.192	3.15	2.05	3.77	0.021	<0.01	0.3
Iron total	mg/L	0.213	3.34	2.1	3.81	0.0	NM	0.3
Manganese dissolved	mg/L	0.025	0.194	0.121	0.215	0.012	NM	0.05
Manganese total	mg/L	0.025	0.188	0.120	0.216	0.012	<0.01	0.05

Table 4-1. Summary of Field and Laboratory Water Quality Test Results
Data Collection Results

Sample ID Test Info Constituent	Units	SWR_NPW1 24 Hr CRT 8/4/2016	SWR-NP012 Packer Test #1 (bottom zone) 8/11/2016	SWR-NP023 Packer Test #2 (middle zone) 8/17/16	SWR-NP034 Packer Test #3 (upper zone) 8/23/16	BAC Pilot Eff. Pilot test at York River5 8/5/16	RO Pilot test at York River6 8/5/16	Primary & Secondary MCL7
Magnesium total	mg/L	3.95	31.9	19.30	35.90	8.30	<0.01	
Potassium total	mg/L	12.4	36.1	28.0	36.1	14.0	0.3	
Sodium total	mg/L	488	1590	1270	1740	118	2.9	50
Calcium total	mg/L	8.99	67.8	41	77	52	0	
Sulfate	mg/L	55.5	195	151	208	93	<1.0	250
Chloride	mg/L	514	2550	1970	2760	151	<4.0	250
Alkalinity as CaCO ₃	mg/L	373	275	299	248	110	<0.1	
Nitrate/Nitrite-N	mg/L	<0.01	<0.02	<0.02	<0.01	2.02	0.302	
Nitrate as N	mg/L	<0.01	<0.02	<0.02	<0.01	2.72	0.47	10
Total Kjeldahl Nitrogen	mg/L	<0.5	1.09	0.74	1.19	1.19	<0.50	
Fluoride	mg/L	3.05	0.43	0.52	0.41	0.57	<0.1	2.0
Silica as SiO ₂	mg/L	24.7	44.4	44.7	44.9	NM	0.2	
Silicon as Si	mg/L	11.5	20.7	20.9	21.0	NM	0.1	
Dissolved organic carbon	mg/L	0.15	0.06	<0.1	<0.2	1.8	0.33	
Total organic carbon	mg/L	0.17	<0.05	<0.1	<0.1	2.000	0.48	
Total phosphorus	mg/L	0.32	0.11	0.12	0.09	0.05	0.10	
Ortho-phosphate	mg/L	0.34	0.02	0.02	0.02	0.05	<0.02	
Total dissolved solids	mg/L	1370	4830	3820	5160	525	20	500
Total suspended solids	mg/L	<1.0	4	<1.0	6	NM	NM	
Hardness	mg/L CaCO ₃	38.7	301	183	341	NM	NM	250
Ammonia	mg/L	0.39	0.98	0.79	0.62	0.01	0.57	
BOD5	mg/L	<2	<2	<2	<2	NM	NM	
COD	mg/L	<3	<18	<12	11	7.2	5	

Table 4-1. Summary of Field and Laboratory Water Quality Test Results
Data Collection Results

Sample ID Test Info Constituent	Units	SWR_NPW1 24 Hr CRT 8/4/2016	SWR-NP012 Packer Test #1 (bottom zone) 8/11/2016	SWR-NP023 Packer Test #2 (middle zone) 8/17/16	SWR-NP034 Packer Test #3 (upper zone) 8/23/16	BAC Pilot Eff. Pilot test at York River5 8/5/16	RO Pilot test at York River6 8/5/16	Primary & Secondary MCL7
Gross Alpha		NM	NM	10	11	NM	NM	15
Gross Beta	pCi/L	NM	23	19	21	NM	NM	4
Ra 226 + Ra 228	pCi/L	NM	6.2	1.8	6.1	NM	NM	5
Uranium	µg/L	NM	<2.0	<5.0	<1.0	NM	NM	30
Calculated Species								
Ionic Strength	mol/L	0.0235	0.083	0.0649	0.089	0.019	0.00017	

Notes:

- ¹ Groundwater sample collected near end of 24-hour pumping constant rate test (CRT)
- ² Groundwater sample collected from LPA during Packer Test
- ³ Groundwater sample collected from MPA during Packer Test
- ⁴ Groundwater sample collected from UPA during Packer Test
- ⁵ RO = reverse osmosis – mean of daily and weekly samples
- ⁶ BAC = biologically activated carbon – mean daily and weekly samples collected after GAC and UV

CaCO₃ = calcium carbonate

eq = equivalent

ID = identification

mol/L = mole per liter

NM = not measured

pCi/L = picocurie(s) per liter

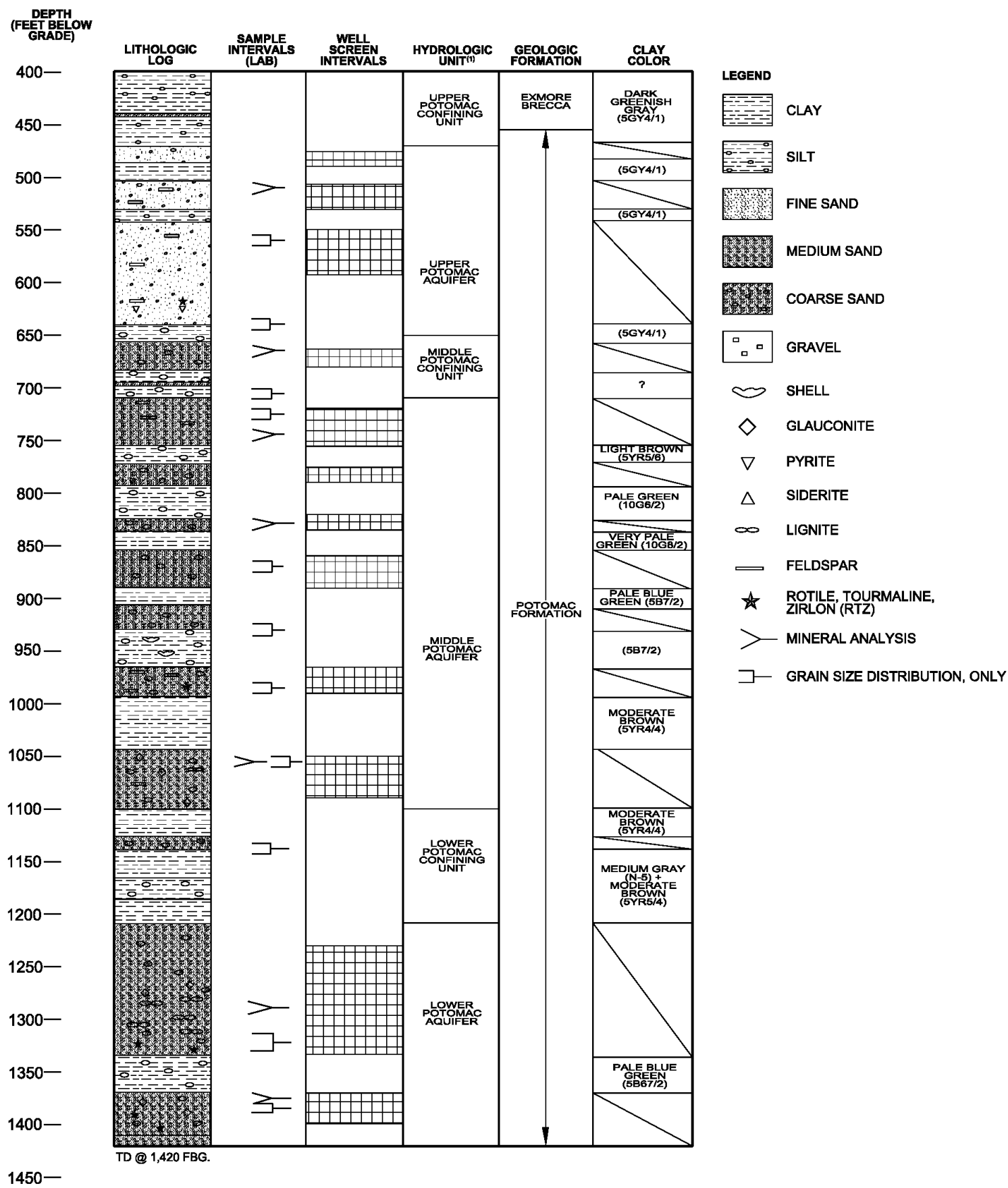


Figure 4-3. Lithologic Log in PAS Nansemond TW-1
Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

Evaluating Geochemical Compatibility

This section presents observations based on data collected and evaluates the geochemical compatibility issues related to the following:

- Mineral dissolution
- Mineral precipitation
- Clay structure fragmentation
- Clay particle dispersion

Based on the results, potential mitigation approaches will be identified and evaluated for effectiveness.

5.1 Data Observations

5.1.1 Recharge Water Data Observations and Discussion

Samples of the membrane-based and carbon-based recharge water were collected at a frequency varying from daily to bi-weekly, resulting in multiple concentrations for a single analyte. For this analysis, the mean of individual analytes was calculated and appear in Table 4-1.

5.1.1.1 Membrane-Based Process Recharge Water Observations and Discussion

Recharge treated by the membrane-based process exhibited the following:

- A slightly acidic pH (6.0)
- Dilute TDS (20 mg/L) slightly greater than rain water
- A low ionic strength (0.00017)
- Cations and anions in the influent were reduced following the treatment process, resulting in concentrations of cations including calcium (Ca), magnesium (Mg), and potassium (K) falling below 1.0 mg/L, with sodium (Na) concentrations approaching 3 mg/L
- Concentrations of anions comprising phosphate (<0.02 mg/L), chloride (<4.0 mg/L), alkalinity (<0.1 mg/L) and sulfate (<1 mg/L) fell below their respective MDLs
- In evaluating data at concentrations below MDLs, a convention employing one half the MDL was applied
- Membrane-based recharge water displayed a sodium chloride water type (Figure 5-1)
- Common trace metals including iron and manganese exhibited concentrations less than MDLs
- Membrane-based has limited effect on DO concentrations in the recharge, which at 5 mg/L fell in the oxic range (DO > 2.0 mg/L). Consistent with oxic concentrations of DO, the recharge displayed an oxidizing potential (oxidation-reduction potential [ORP] > 300 millivolts [mV]) measurement (Figure 5-2, Tables 5-1 and 5-2)
- Concentrations of nutrients varied between less than MDL's for total phosphorous and ortho-phosphate as P to less than MDLs to 0.47 mg/L for Total Kjeldahl Nitrogen and nitrate, respectively
- Total and dissolved organic carbon concentrations were nearly equal at 0.48 and 0.33 mg/L, respectively

5.1.1.2 Carbon-based Recharge Water Observations and Discussion

Recharge treated by the carbon-based process exhibited the following:

- A circum-neutral pH (6.96)
- Slightly brackish TDS (525 mg/L)
- Ionic strength (0.019)
- Similar to the chemistry of membrane-based recharge water, carbon-based recharge water displayed a sodium chloride water type (Figure 5-1)
- Iron and manganese exhibited concentrations slightly exceeding their MDLs (0.01 mg/L) at 0.021
- 0.012 mg/L, respectively. Iron and manganese concentrations appeared sufficiently low as to not present a concern for creating TSS in the recharge. Concentrations of either trace metal above 0.1 mg/L, or together approaching 0.1 mg/L can produce sufficient amounts of TSS to clog a recharge well
- With the exception of nitrate (2.72 mg/L), concentrations of nutrients fell below MDLs
- Concentrations of total organic carbon (TOC) (2 mg/L) were about the same as the dissolved organic carbon (1.8 mg/L)
- DO concentrations ranged from 16 to 18 mg/L exhibiting an oxidizing ORP

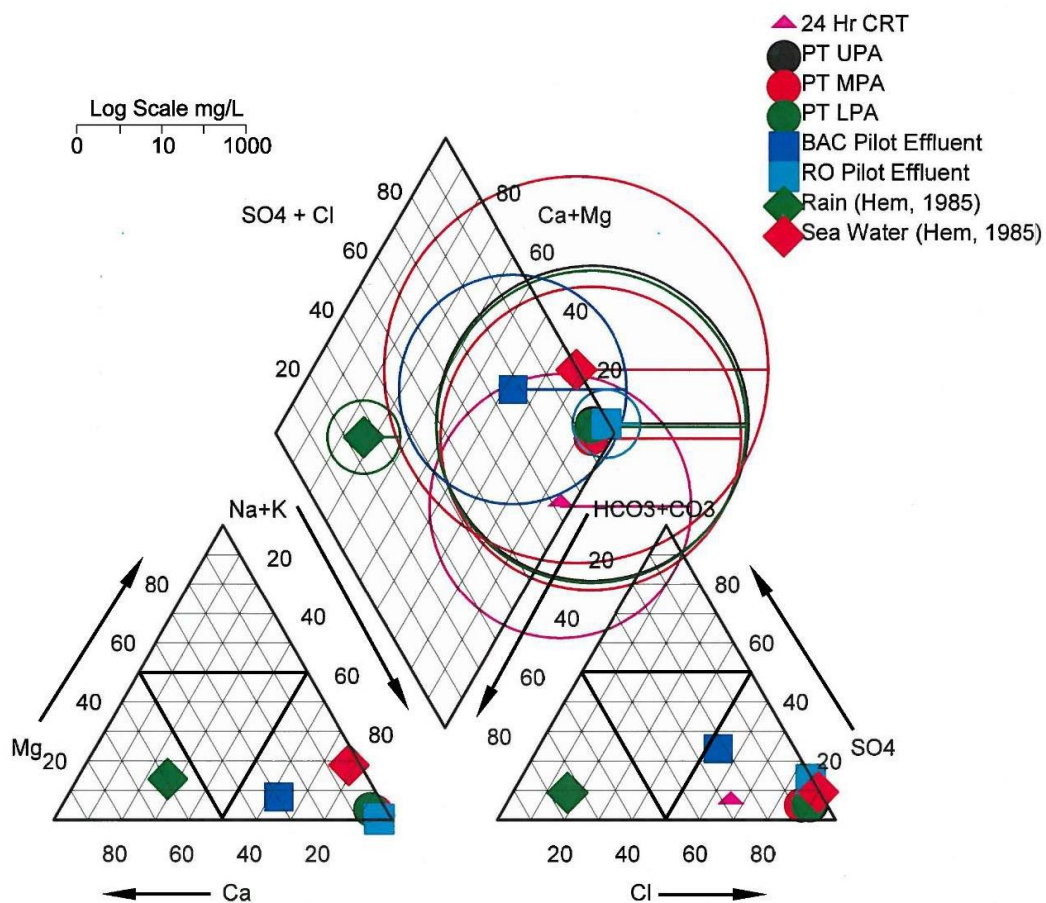


Figure 5-1. Piper Diagram of Cation-Anion Chemistry of Recharge water and Native Groundwater from PAS
Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads
Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

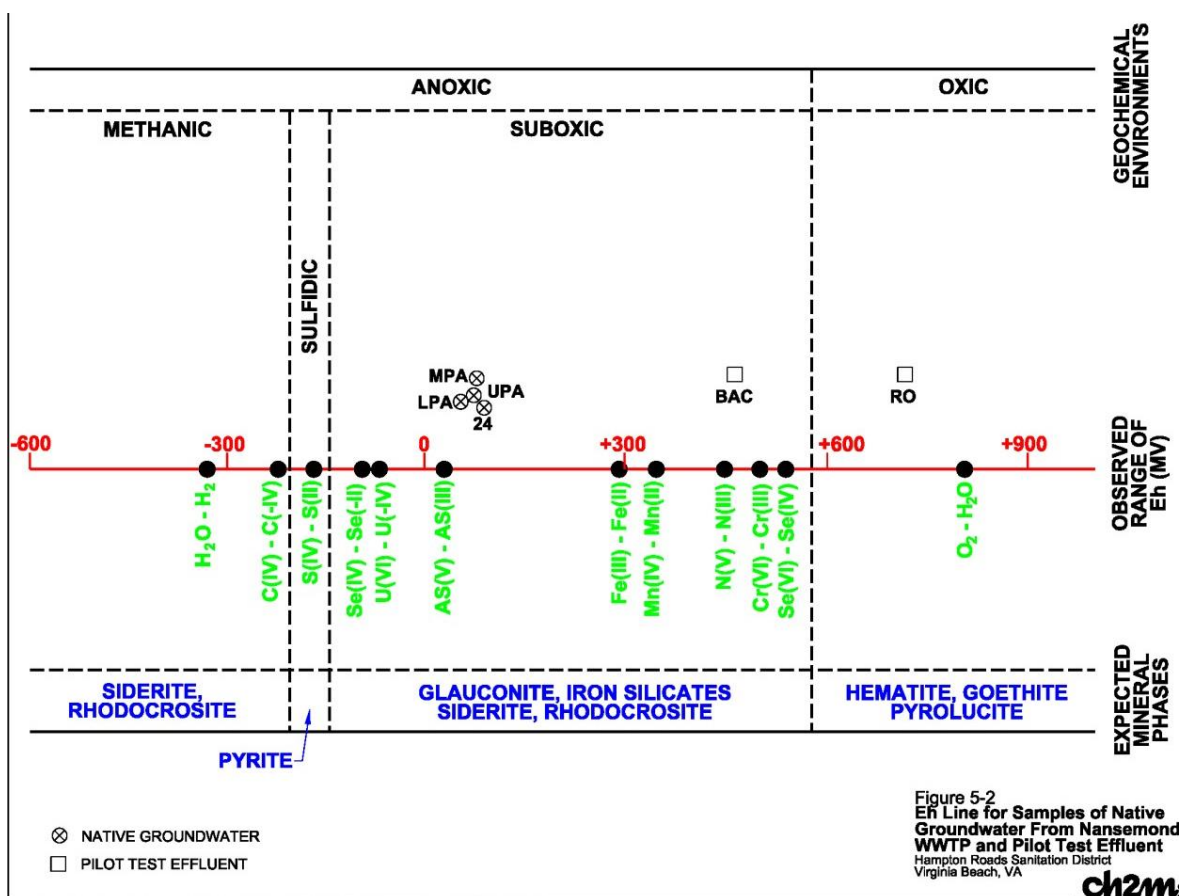


Figure 5-2. Eh Line for Samples of Native Groundwater from Nansemond WWTP and Pilot Test Recharge water
Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

Table 5-1. Criteria and Threshold Concentrations for Identifying Redox Processes in Groundwater

Redox category	Redox process	Electron acceptor (reduction) half-reaction	Dissolved oxygen (mg/L)	Nitrate, as nitrogen (mg/L)	Manganese (mg/L)	Iron (mg/L)	Sulfate (mg/L)	Iron/sulfide (mass ratio)
Oxic	O ₂	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	≥0.5	—	<0.05	<0.1	—	
Suboxic	Suboxic	Low O ₂ ; additional data needed to define redox process	<0.5	<0.5	<0.05	<0.1	—	
Anoxic	NO ₃	$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2(g) + 6H_2O$; $NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$	<0.5	≥0.5	<0.05	<0.1	—	
Anoxic	Mn(IV)	$MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	<0.5	<0.5	≥0.05	<0.1	—	
Anoxic	Fe(III)/SO ₄	Fe(III) and (or) SO ₄ ²⁻ reactions as described in individual element half reactions	<0.5	<0.5	—	≥0.1	≥0.5	no data
Anoxic	Fe(III)	$Fe(OH)_3(s) + H^+ + e^- \rightarrow Fe^{2+} + H_2O$; $FeOOH(s) + 3H^+ + e^- \rightarrow Fe^{2+} + 2H_2O$	<0.5	<0.5	—	≥0.1	≥0.5	>10
Mixed(anoxic)	Fe(III)-SO ₄	Fe(III) and SO ₄ ²⁻ reactions as described in individual element half reactions	<0.5	<0.5	—	≥0.1	≥0.5	≥0.3, ≤10
Anoxic	SO ₄	$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$	<0.5	<0.5	—	≥0.1	≥0.5	<0.3
Anoxic	CH ₄ gen	$CO_2(g) + 8H^+ + 8e^- \rightarrow CH_4(g) + 2H_2O$	<0.5	<0.5	—	≥0.1	<0.5	

[Table was modified from Jurgens et al, 2009. Redox process: O₂, oxygen reduction; NO₃, nitrate reduction; Mn(IV), manganese reduction; Fe(III), iron reduction; SO₄, sulfate reduction; CH₄gen, methanogenesis. Chemical species: O₂, dissolved oxygen; NO₃⁻, dissolved nitrate; MnO₂(s), manganese oxide with manganese in 4+ oxidation state; Fe(OH)₃(s), iron hydroxide with iron in 3+ oxidation state; FeOOH(s), iron oxyhydroxide with iron in 3+ oxidation state; SO₄²⁻, dissolved sulfate; CO₂(g), carbon dioxide gas; CH₄(g), methane gas. Abbreviations: mg/L, milligram per liter; —, criteria do not apply because the species concentration is not affected by the redox process; ≤, less than or equal to; ≥, greater than or equal to; <, less than; >, greater than]

Table 5-2. Results of Analysis with USGS Redox Program

Redox Variables									Redox Assignment		Fe ²⁺ /Sulfide	Eh	TOC
Sample ID	Units	Dissolved O ₂	NO ³⁻ (as Nitrogen)	Mn ²⁺	Fe ²⁺	SO ₄ ²⁻	Sulfide (sum of H ₂ S, HS, S ²⁻)	No. of Params	General Redox Category	Redox Process	ratio	(mV)	(mg/L)
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)						
24 Hour Pump Test		0.07	0.005	0.025	0.12	56	0.02	6	Mixed(anoxic)	Fe(III)-SO4	6.00	97	0.15
Packer Test - UPA		0.2	0.01	0.22	3.2	208	0.01	6	Anoxic	Fe(III)	320.00	58	0.01
Packer Test - MPA		0.3	0.01	0.12	2.4	151	0.005	6	Anoxic	Fe(III)	480.00	67	0.1
Packer Test - LPA		0.125	0.02	0.19	3.2	195	0.005	6	Anoxic	Fe(III)	640.00	50	0.025
BAC Pilot Recharge water		17	2.7	0.012	0.02	93	0.005	6	Oxic	O2		471	1.8
RO Pilot Recharge		5	0.5	0.005	0.005	0.5	0.005	6	Oxic	O2		725	0.3

Eh in mV calculated by adding 200 mV to field measured ORP values.

5.1.2 Groundwater Data Observations and Discussion

The PAS consists of Upper, Middle and Lower zones. Zone isolation (packer) testing was conducted to collect water quality and hydraulic data from each of these PAS zones. These data are discussed below.

5.1.2.1 Upper Potomac Aquifer Data Observations and Discussion

Groundwater sampled during packer testing of the UPA (Packer Test #3) displayed an anomalous chemistry showing TDS (5,160 mg/L), chloride (2,760 mg/L) and sodium (1,740 mg/L) exceeding concentrations of the same constituents in the MPA and LPA. Research has demonstrated that TDS and chloride concentrations increase at rates of 410 and 270 mg/L per 100 feet of depth, respectively in the PAS (RIK, 2000). Thus, concentrations should increase in the MPA and LPA compared to the UPA. Moreover, TDS concentrations in a sample collected at the end of the 24-hour constant rate test equaled 1,370 mg/L, at least 1,400 mg/L less than concentrations displayed from UPA, MPA, and LPA during the packer testing.

The anomalous concentrations probably originate from a single sand interval positioned near the base of the UPA adjacent to the pump intake during the packer test. This relationship often appears in monitoring wells screening the individual sand intervals of the PAS. Since its deposition, saline water has transgressed and receded in the PAS, often stranding zones of saltier water near the bottom of aquifer units containing fresh water.

The appearance of the anomalous chemistry benefits HRSD's testing program by revealing the heterogeneity of chemistry across the individual sand units and will help tailor the packer testing scheme at HRSD's other WWTPs. To detect these anomalous chemistries at individual sand intervals, the packer intervals will get shortened to 50 feet or less. Detecting the saltier intervals will prove important for developing schemes to condition clay minerals in the individual aquifer units.

The dilute chemistry displayed by the sample from the 24-hour aquifer test in comparison to samples from the MPA and LPA suggests that groundwater from the bulk chemistry UPA is significantly more dilute than exhibited by the sample from the packer test. An attempt to approximate the bulk chemistry of the UPA was executed using a mass balance approach based on the transmissivity of each PAS aquifer interval, determined by the packer testing (Table 5-3). Using this approach, the transmissivity of the UPA, MPA, and LPA determines the proportion of groundwater each aquifer unit contributed to the sample collected at the end of the 24-hour constant rate aquifer test.

Table 5-3. Summary of Transmissivity from Packer Testing at TW-1

Aquifer	Transmissivity ¹ (square feet/day)	Contribution (%)
Upper Potomac Aquifer	2,800	41
Middle Potomac Aquifer	2,600	38
Lower Potomac Aquifer	1,400	21

Note:

¹ Average of several analytical methods

Based on the foregoing, the approximated UPA exhibited the following:

- A circum-neutral pH
- TDS concentrations (514 mg/L) slightly greater than the secondary MCL (SMCL) of 500 mg/L
- Relatively low iron (0.08 mg/L) and manganese (0.01 mg/L) concentrations
- Similar to the chemistry of the carbon-based recharge water, an ionic strength around 0.019

- A sodium chloride water type (Figure 5-1).
- Fluoride, a constituent often exceeding the primary maximum contaminant limit in the PAS, was slightly greater than 1.0 mg/L. The elevated value observed in the sample collected during the 24-hour constant rate aquifer test likely originated from the UPA.
- Groundwater measured during the UPA packer test exhibited a transitional ORP (Figure 5-2), falling in the anoxic redox category with ferric iron reduction as the predominating redox process (Table 5-2).

5.1.2.2 Middle Potomac Aquifer Data Observations and Discussion

The MPA exhibited the following:

- A circum-neutral pH
- Brackish concentrations of TDS (3,820 mg/L)
- An ionic strength of 0.065
- A sodium chloride water chemistry (Figure 5-1)
- Iron (2.1 mg/L) and manganese (0.12 mg/L) concentrations exceeded the SMCL of 0.3 and 0.05 mg/L, respectively
- Nutrient (Total Kjeldahl Nitrogen, nitrate, total phosphorus and ortho-phosphate) fell below or just at their respective MDLs
- TOC concentrations fell below or just at their respective MDLs
- Similar to the sample collected during packer testing in the UPA, groundwater from the MPA displayed a transitional ORP, returning an anoxic redox category with ferric iron reduction as the prevailing redox process (Table 5-2).

5.1.2.3 Lower Potomac Aquifer Data Observations and Discussion

The LPA exhibited the following:

- Similar to samples collected in the UPA and MPA, the LPA exhibited a circum-neutral pH
- Brackish concentrations of TDS (4,830 mg/L)
- An ionic strength of 0.083
- A sodium-chloride chemistry (Figure 5-1)
- Iron (3.2 mg/L) and manganese (0.19 mg/L) exceeded the SMCL
- Nutrient (Total Kjeldahl Nitrogen, nitrate, total phosphorus and ortho-phosphate) concentrations fell below or just at their respective MDLs
- TOC concentrations fell below or just at their respective MDLs
- Similar to the samples collected during packer testing in the UPA and MPA, groundwater from the LPA displayed a transitional ORP, returning an anoxic redox category with ferric iron reduction as the prevailing redox process (Table 5-2)

5.1.2.4 Summary of PAS Groundwater Observations and Discussion

The groundwater from the three PAS aquifers exhibited similar chemistries, with increasing chloride and sodium concentrations, boosting the ionic strength with depth. Chloride in the samples from each aquifer exhibited concentrations significantly greater than encountered in the recharge. An inert constituent that migrates at the velocity of groundwater, chloride makes an excellent tracer for tracking

the movement of recharge in an aquifer. The disparity in concentrations will enhance chloride's sensitivity in its application as a tracer constituent.

5.1.3 Lithology Data Observations and Discussion

This section describes the lithology and CEC of the minerals composing the PAS. Core samples from the UPA, MPA, and LPA fell into three categories comprising:

- Aquifer sands
- Silty mudstone, confining beds
- Clay-rich aquifer sands

The clay-rich aquifer sand samples resembled confining bed sediments when selected for mineralogical analysis. The quartz-rich aquifer sand samples appeared grain supported and classified as sub-arkosic (Figure 5-3), a term describing sands containing proportionally high abundances of the mineral, feldspar. Framework grains were dominated by quartz, feldspar, and modest amounts of lithic (rock fragments) material, composed mostly of granite fragments. Feldspar grain populations consisted mostly of microcline (potassium-rich) with minor amounts of albite (sodium rich; Table 5-4).

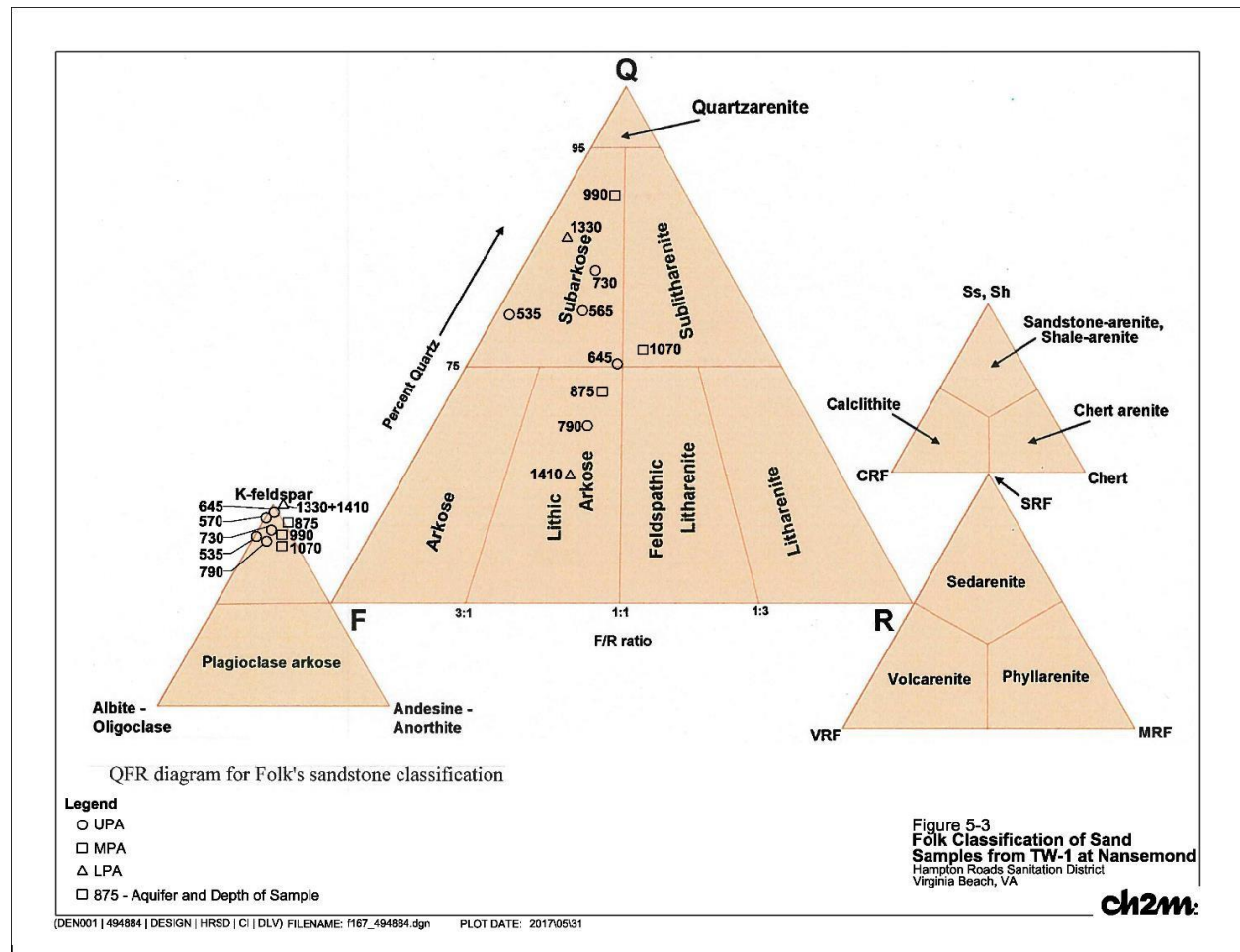


Figure 5-3. Folk Classification of Sand Samples from TW-1 at Nansemond
Evaluating the Compatibility of Recharge water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads
Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

Table 5-4. Summary of X-Ray Diffraction Results on Samples from TW-1

Sample Depth and		465-475	525-535	555-565	635-645	700-710	720-730	780-790	865-875	925-935	980-990	1020-1030	1060-1070	1145-1155	1315-1330	1440-1410
Hydrostratigraphic Unit		CBIC above UPA	UPA	UPA	UPA	MPA Confining Unit	MPA	MPA	MPA	MPA (clay unit)	MPA	MPA (clay unit)	MPA	LPA Confining Unit	LPA	LPA
Mineral	Chemical Forumla	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Quartz	SiO ₂	23	81	83	79.5	54	73	64	80	62	82	24	81	54	82	76
Albite	(Na, Ca) AlSi ₃ O ₈	2	2	1	0.5	1.5	2	2	1	1	0.5	1	0.5	8		
Microcline	KAlSi ₃ O ₈	2	12	13	15	9	15	17	15	9	13	5	12	8	11	16
Quartz and Feldspar	Total	27	95	97	95	64	.5	90	83	96	72	95	.5	3	0	93
Calcite	CaCO ₃	24	1	0.5	1	2	1	1.5	0.5	1	0.5	3	0.5	1	1.5	2
Ferroan Dolomite	Ca(Mg _{0.67} Fe _{0.33})(DO ₃) ₂		0.15	0.15	0.5	0.5	0.5	0.5	0.15				0.5	1	0.5	1
Gypsum	CaSO ₄ 2H ₂ O	0.5										1				
Siderite	FeCO ₃											1				
Pyrite	FeS ₂	3				0.15	0.5			0.15						
Magnetite	Alpha Fe ₃ O ₄		0.5	0.5	0.5		0.5	0.5	0.5		0.5		1	0.25	0.5	1
Akaganite	Beta FeOOH	1	0.5	0.5			1									
Clinoptilite	((Na,K,Ca) ₆ (Si,Al) ₃₆ O ₇₂ 2H ₂ O				0.15											
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	5	0.5	0.5	0.7	6	0.5	3.5	0.5	6	1	14	1	5	1	1
Chlorite	(Mg, Al) ₆ (Si, Al) ₄ O ₁₀ (OH) ₈	5.5	0.5	0.15		1				0.25			0.25	1		0.25
Illite/Mica	KAl ₂ (Si ₃ AlO ₁₀)(OH) ₂	7	1	0.15	0.3	7	0.5	1	0.5	3	0.5	8	0.5	3	0.5	0.5
Montmorillonite	((Na,K,Ca) ₆ (Si, Al) ₃₆ O ₇₂ 2H ₂ O		1		2	19	6	10	2	18	2	43	3	18	3	2.5
Mixed-layer illite smectite	K _{0.5} Al ₂ (Si, Al) ₄ O10(OH) ₂ 2H ₂ O	27		1												
Clay	Total %	44.5	3	1.8	3	33	7	14.5	3	27.25	3.5	65	4.75	27	4.5	4.25
Total		100	100.15	100.45	100.15	100.15	100.5	100	100.15	100.4	100	100	100.25	99.25	100	100.25

Clay minerals were encountered in the pore spaces (interstitial) of the aquifer sands as grain coating or pore filling. Often detrital clay was mixed with silt and iron oxide crystals. Detrital clay describes clay particles deposited with the sands while authigenic clays precipitate after deposition. In the PAS, authigenic clays typically form after the dissolution of feldspars.

The clay content of the aquifer sand samples as determined from XRD and grain size distribution (GSD) analysis ranged between 1 and 14 percent with most less than 5 percent (Table 5-5). Interstitial clay mineralogy was dominated by montmorillonite, with subordinate amounts of kaolinite, and traces of chlorite (Table 5-6; Figure 5-4).

Table 5-5. Average Interstitial Clay Content of PAS

Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

Sample Interval (feet below grade)	Aquifer	Analysis Type	Clay content (%)	Average Interstitial Clay Content Each Aquifer (%)
505 to 515	UPA	GSD	3	
525 to 535	UPA	XRD	3	
555 to 565	UPA	XRD	1.8	
635 to 645	UPA	XRD	3	
670 to 680	UPA	GSD	1	
720 to 730	UPA	XRD	7	
740 to 750	UPA	GSD	2	
780 to 790	UPA	XRD	14	4.35
825 to 835	MPA	GSD	7	
865 to 875	MPA	XRD	3	
980 to 990	MPA	XRD	3.5	
1050 to 1060	MPA	GSD	5	
1060 to 1070	MPA	XRD	4.75	4.65
1285 to 1295	LPA	GSD	1	
1315 to 1330	LPA	XRD	4.5	
1370 to 1380	LPA	GSD	1	
1400 to 1410	LPA	XRD	4.25	2.69

Notes:

UPA - 505 to 790 fbg

MPA - 820 to 1,090 fbg

LPA - 1,230 to 1,410 fbg

Table 5-6. Clay Mineralogy in Aquifer Sands and Confining Beds

Mineral	Chemical Formula	466 to 475 CB above UPA Normal to 100%	CB in UPA Normal to 100%	Average UPA aquifer sands Normal to	CB in MPA Normal to 100%	Average MPA aquifer sands Normal to	Average LPA aquifer sands	Average PAS ALL Normal to 100%
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	11.2	18.2	19.8	21.5	22.1	22.9	20.9
Chlorite	$(\text{Mg}, \text{Al})_6(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_8$	12.4	3.0	5.1	0.0	1.8	2.9	2.6
Illite/Mica	$\text{KAl}_2(\text{Si}_3\text{AlO}_{10})(\text{OH})_2$	15.7	21.2	13.1	12.3	13.8	11.4	14.4
Montmorillonite	$((\text{Na}, \text{K}, \text{Ca})_6(\text{Si}, \text{Al})_{36}\text{O}_{72} \cdot 2\text{H}_2\text{O})$	0.0	57.6	50.9	66.2	62.3	62.7	59.9
Mixed-layer illite smectite	$\text{K}_{0.5}\text{Al}_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$	60.7	0.0	11.1	0.0	0.0	0.0	2.2

Notes:

CB = confining bed

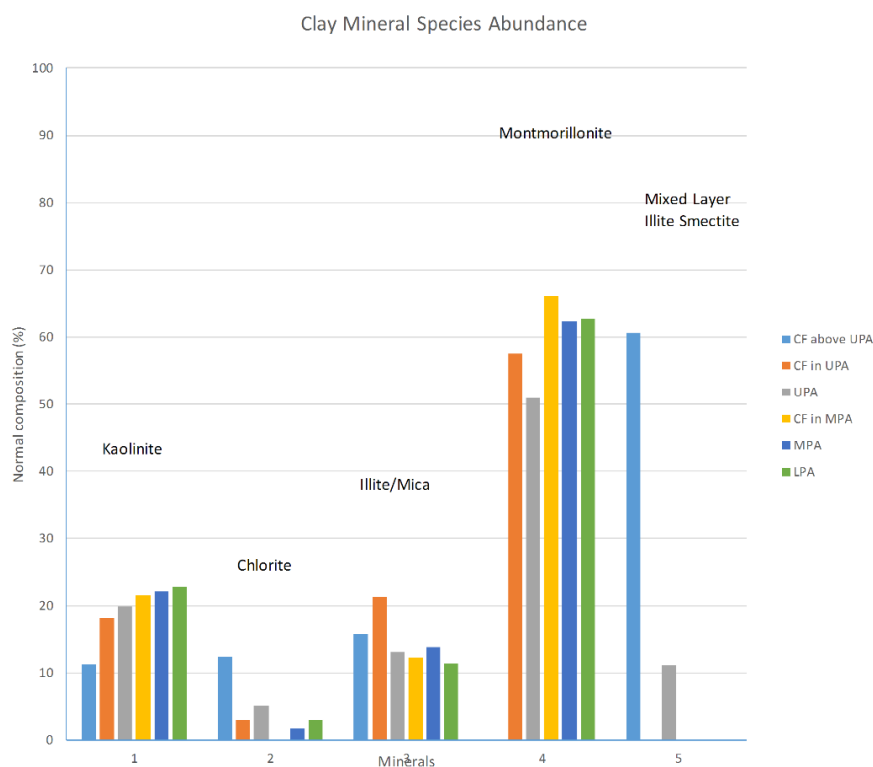


Figure 5-4. Clay Mineralogy in Aquifer Sand and Confining Bed Samples

Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

The silty mudstone confining units (470 and 1,030 fbg) were each characterized by 44 to 65 percent detrital clay combined with quartz and feldspar grains. Similar to the mineralogy of the interstitial clays, both confining unit samples consisted of from greatest to least abundant: montmorillonite, kaolinite, and illite. The samples originating from 470 fbg displayed a dark-gray color, while the sample from 1,030 fbg was brick red. The bright red coloring often originates from subaerial exposure and the oxidation of iron-bearing minerals, shortly after burial. The clay mineral suite encountered in one sample near the top of the section (475 fbg) was dominated by mixed layers of illite and smectite, instead of montmorillonite, and exhibited a dark gray color. This sample probably originated in a unit independent of the PAS like the Yorktown Formation or the Exmore Breccia.

The clay-rich, aquifer sands (710, 935, and 1,155 fbg.) comprised a grain-supported matrix with pore spaces filled with detrital clays. Similar to other samples, the clay minerals in order of abundance comprised montmorillonite, kaolinite, illite and chlorite. The similarity of the clay mineral suites residing in the aquifer sands, confining sediments, and clay-rich aquifer sands supports a detrital origin. A higher abundance of authigenic clays would probably exhibit a more varying mineral suite over the thick PAS section. Similar to the confining beds, the clay-rich sediments contained a greater variety of trace minerals than the aquifer sands.

The presence of montmorillonite as the predominating, interstitial clay mineral in the aquifer sands of the PAS holds mixed tidings for injection operations. Because of its multi-layer structure, montmorillonite suffers significant damage when exposed to recharge containing a significantly lower ionic strength. Conversely, montmorillonite should prove easier to stabilize than other clay minerals through treatments with divalent or trivalent salt solutions.

Exclusive of the clay minerals, all the samples of the aquifer sands contained trace (less than 1 percent) amounts of calcite, magnetite, and akaganeite (iron hydroxide). The iron sulfide mineral, pyrite (FeS_2),

a potential source of iron, manganese, and arsenic if reacting with elevated concentrations of DO contained in recharge, was encountered at trace concentrations in both confining bed samples, and two of the three clay-rich, aquifer sands (710 and 935 fbg). Pyrite was not detected in any of the samples of aquifer sands, by lithologic logging or the microscopic analysis conducted in the mineralogical lab. When contained in confining beds or the clay fraction of aquifer sands, pyrite should not come in contact with recharge.

Siderite, an iron carbonate (FeCO_3) that can release large amounts of iron in the presence of DO, was found in one of the confining bed samples (1,030 fbg).

As samples collected represented a small fraction of the PAS, the absence of pyrite and siderite in the mineralogical analysis may result from sample distribution. Because their importance to MAR operations, both minerals were considered present at percentage levels and treated in geochemical modeling simulations.

5.1.3.1 Summary of Lithological Information

In summary, PAS aquifer sands consisted of greater than 90 percent framework grains consisting of quartz and orthoclase feldspar. Reactive metal bearing minerals like pyrite and siderite were encountered only in confining beds or fine-grained units within the aquifer sands. If relegated to only the finer grained portions of the aquifer, these minerals should not present a concern for injection operations. However, the samples represent only a small portion of the aquifer section. In maintaining a conservative approach, evaluations of aquifer compatibility must assume that these minerals may occur in aquifer sand intervals.

Although interstitial clay minerals comprise less than 5 percent of the aquifer matrices, the greatest concern to injection operations involves the predominance of the clay mineral, montmorillonite. Montmorillonite can swell or fragment in the presence of recharge containing exchanging cations or lower ionic strength.

Conversely, montmorillonite has proven to be the clay mineral that is most easily conditioned through treatments with divalent or trivalent salt solutions.

5.2 Mineral Dissolution/Precipitation Evaluation

5.2.1 Evaluation Results Mixing Between Recharge Water and Native Groundwater

Mixing during injection operations will typically involve mixing between the recharge water and native groundwater as the recharge volume increases in the PAS. An interface will form between the two water types that migrates away from the injection well. Although TW-1 was screened across all three aquifers of the PAS, operational MAR wells will probably screen only one or two PAS aquifers. Thus, mixing in the borehole between native groundwater of the UPA, MPA, and LPA should not create a significant concern.

As described, mixing reactions prove most troublesome around the injection wellbore. One common reaction involves the precipitation of oxide minerals when recharge containing DO contacts dissolved iron or manganese entrained in the recharge or native groundwater. Both recharge waters contained measurable concentrations of DO, and no dissolved iron and manganese concentrations. Conversely, native groundwater exhibited anoxic concentrations of DO ($\text{DO} < 1.0 \text{ mg/L}$) but concentrations of reduced iron and manganese, ranging between 0.1 to 3.2 mg/L and 0.03 to 0.22 mg/L, respectively. Other minerals like calcite and siderite can also precipitate during mixing.

5.2.1.1 Mixing Modeling

To evaluate mixing between the differing water types, recharge water (membrane-based and carbon-based) and groundwater, PHREEQC was used to simulate mixing between the recharge and native groundwater chemistries at a 1:1 ratio. With the recharge and native groundwater at equal proportions, the 1:1 ratio usually produces the most conservative geochemical results. The modeling included mixing membrane-based and carbon-based with the native groundwater from the UPA (packer test), UPA (estimated from Section 3), MPA, and LPA.

Important reactions tracked during the mixing simulations included the potential precipitation of metal oxide, hydroxide, sulfate, and carbonate minerals along with dissolution of silicates, including clays. Because of the bulk chemistry of the two recharge waters and native groundwater from the UPA, MPA, and LPA, potential mineral suites identified by PHREEQC in the mixed water and their SIs were repeated across the eight mixtures.

5.2.1.2 Mineral Precipitation/Dissolution Evaluation

The SI of a mineral (Langmuir, 1997) determines whether the mineral occurs in equilibrium ($SI=0.0$) with a mixed water chemistry; is under saturated ($SI<0.0$) and should dissolve if present; or is supersaturated ($SI>0.0$) and should precipitate. Estimation of SIs are usually not exact, often varying over ± 0.3 units, depending on the composition of the solution. The SI provides a guideline on how minerals will behave in a water sample.

Table 5-7 lists common minerals and their weathering products identified in eight combinations of mixed water. To prevent dissolving reactive metal bearing minerals in the PAS aquifers, the pH of membrane-based and carbon-based were adjusted to 7.8, resulting in alkalinity concentrations of 2 and 129 mg/L, respectively. In mixtures involving membrane-based recharge water and groundwater from the PAS, the pH of the mixed water fell from 7.8 to around 7.1. Quartz, the most common mineral in the aquifer sand of the PAS returned one slightly under-saturated SI (UPA estimated) and the remainder over saturated SI ($SI= 0.46$ to 0.74) for the four simulations. Oversaturation of quartz and near-equilibrium SIs for less crystalline forms of silica such as chalcedony and cristobalite indicates feldspars are dissolving, releasing silica. Gibbsite ($Al(OH)_3$) appeared oversaturated in the mixed water consistent with the dissolution of feldspar, and precipitation of residual byproducts in a weathered environment.

To simulate redox conditions found in the groundwater samples, DO concentrations and the Eh measurement input into PHREEQC were based on samples collected during packer testing (Table 5-2). Other minerals potentially reacting in the mixing waters between membrane-based recharge water and the PAS aquifer included the carbonates, comprising calcite, aragonite, and siderite. Calcite ($CaCO_3$) appeared uniformly undersaturated ($SI -0.62$ to -1.97) in all the mixed waters suggesting it will not precipitate. Calcite in an undersaturated condition during mixing benefits recharge operations by not precipitating, blocking pore spaces, and reducing the permeability of the aquifer. Aragonite, an isomorph of calcite showed similar indices, ranging from -0.76 to -2.11 . The iron carbonate mineral ($FeCO_3$), siderite, displayed SI values similar to calcite and aragonite with strongly undersaturated indices ranging from -7.15 to -10.32 .

Other important minerals included gypsum and jarosite, a weathering product of iron-bearing minerals and sulfides. Jarosite displayed both over- and undersaturated SI values from -5.99 to 0.69 . Similar to the carbonates, gypsum exhibited undersaturated indices ranging from -2.13 to -4.01 , respectively.

Other than the resulting pH, mixing carbon-based recharge water with native groundwater from the PAS rendered very similar mineral SIs to membrane-based recharge water mixtures. With its greater buffering capacity, the pH of carbon-based recharge water mixed with groundwater ranged between 7.26 and 7.36. Quartz displayed slightly greater oversaturated SI values ranging from 0.46 to 0.74. Common carbonate minerals including calcite, aragonite, and siderite displayed uniformly

undersaturated SI values. Jarosite exhibited undersaturated and near equilibrium SI values from carbon-based recharge water mixtures involving the estimated chemistry from the UPA and MPA, respectively, while, mixtures comprising carbon-based recharge water and the UPA (packer test) and LPA showed oversaturated SI values. Gibbsite a weathering byproduct of feldspars and clay minerals exhibited oversaturated SI values.

Table 5-7. Summary of Mineralogical Results
Simulating Mixing Between Recharge and Native Groundwater Evaluating the Compatibility of Recharge water, Native Groundwater, an d Aquifer Mineralogy at the Hampton Roads Sanitation District’s Nansemond Wastewater Treatment Plant, Test Well 1

Recharge water	Groundwater	pH (standard units)	Siderite (SI)	Quartz (SI)	Aragonite (SI)	Calcite (SI)	Gypsum (SI)	Pyrolusite (SI)	Rhodochrosite (SI)	Gibbsite (SI)	Kaolinite (SI)	Smectite-Ca (SI)	Kmica (SI)	Jarosite(ss) (SI)
RO	UPA est	7.07	-10.32	-0.17	-2.11	-1.97	-4.01	6.25	-2.04	0.93	2.36	-0.28	5.17	-5.99
	UPA Packer Test	7.05	-8.66	0.51	-0.96	-0.82	-2.13	7.21	-0.93	1.12	4.10	2.83	8.33	0.69
	MPA Packer Test	7.11	-7.34	0.51	-0.76	-0.62	-2.19	4.24	-1.00	1.05	3.95	2.68	8.09	-0.27
	LPA Packer Test	7.08	-7.15	0.51	-0.92	-0.78	-2.17	4.30	-0.90	1.10	4.04	2.77	8.28	0.68
BAC	UPA est	7.36	-10.50	0.46	-0.48	-0.34	-2.24	7.53	-1.36	0.64	3.04	1.63	7.07	-4.73
	UPA Packer Test	7.26	-8.95	0.74	-0.39	-0.25	-1.80	8.22	-0.58	0.92	4.16	3.32	8.72	0.59
	MPA Packer Test	7.29	-9.01	0.73	-0.24	-0.10	-1.82	7.97	-0.70	0.88	4.07	3.21	8.71	-0.09
	LPA Packer Test	7.25	-8.82	0.74	-0.37	-0.23	-1.83	8.05	-0.60	0.80	3.90	3.00	8.47	0.73

Notes:
ss = solid solution

5.2.1.3 Summary of Recharge Water/Groundwater Mixing Modeling Results

The modeled precipitation and dissolution relationships show:

- Chemical conditions are present that promote soluble phases of calcite, aragonite, gypsum, and siderite. These constituents will all be undersaturated, preventing precipitation and subsequent clogging of the MAR well.
- Chemical conditions are present that promote the solid phase of other minerals like gibbsite which avoid dissolution and fragmenting and subsequent migration in the aquifer environment and avoids clogging of the MAR well.

Therefore, the resulting recharge water/groundwater mixture chemistries are not anticipated to impact MAR operations. However, PHREEQC was run as an equilibrium model and did not consider reaction kinetics. Thus, these preliminary modeling results may not reflect all conditions governing reactions in the aquifer. Collecting data during MAR operations will better facilitate employing kinetics and transport simulations when running geochemical simulations with PHREEQC.

5.2.2 Evaluation Results Recharge Water and Aquifer Matrix

The recharge water must be evaluated with respect to compatibility with the aquifer matrix, parameters such as DO, metallic bearing minerals and pH interact to mobilize or precipitate constituents resulting in operation and/or water quality problems.

DO in the recharge water can react with reduced metal bearing minerals releasing metals and other constituents, compromising the quality of water injected into the PAS aquifers. DO in the membrane-based recharge water and carbon-based recharge water should range between 5 and 17 mg/L, concentrations recorded during the pilot testing at York River.

Common reduced metal bearing minerals in the PAS aquifers include pyrite and siderite. Results of the analysis of formation samples from test well TW-1 showed no pyrite or siderite in samples of aquifer sands. However, in the PAS, pyrite appeared at amounts ranging up to one percent in confining bed (1,030 fbg) and clay-rich, aquifer sand samples (710 and 935 fbg). Siderite displayed a relative abundance of one percent in only the confining bed sample from 1,030 fbg. Although pyrite and siderite were not encountered in the samples of aquifer sands, large portions of the aquifer sands were not sampled. Thus, simulations for this study assumed these minerals may occur in the aquifer sands.

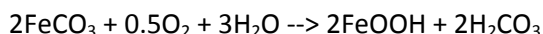
Although ferrous iron represents the primary metal in siderite and pyrite, both minerals can also contain manganese and cadmium. Additionally, pyrite occasionally contains varying amounts of arsenic (Evangelou, 1995).

5.2.2.1 Siderite Dissolution (Iron Mobilization Effect)

Upon encountering DO, Fe II in siderite oxidizes to the ferric (Fe III) ion which hydrolyzes to HFO lowering the pH of the surrounding pore water. The acid created by the HFO precipitation dissolves the soluble mineral. Because of its solubility, at equilibrium, a small amount of siderite can release large amounts of Fe II into the surrounding pore water.

To simulate potential reactions between the recharge water and siderite, PHREEQC was employed to react the maximum concentration of siderite (1 percent) encountered in the samples from TW-1 with membrane-based and carbon-based recharge waters, each containing DO concentrations ranging from 5 to 20 mg/L in

2.0 mg/L increments. The following reaction describes siderite reaction with DO (Postma, 1983):



The reaction releases ferrous iron (not shown in equation) which oxidizes to ferric iron and carbonic acid, lowering the pH of the surrounding pore water, further dissolving the soluble mineral, siderite.

The modeling scenario simulated conservative conditions assuming that siderite concentrations found in confining bed sediments also occur somewhere in the aquifer sands, and that the entire amount encounters DO contained in the recharge stimulating the precipitation of HFO while lowering the pH.

Resulting Fe II at DO concentrations of 20 mg/L ranged from 172 to 300 mg/L for membrane-based and carbon-based recharge waters, respectively (Figure 5-5). Even reacting only 5 mg/L DO with siderite produced Fe II concentrations ranging from 70 to 195 mg/L for membrane-based and carbon-based recharge waters, respectively. To illustrate the full reactive potential of siderite, simulations were performed under conservative conditions allowing the pH to decline during the reaction, increasing the Fe II concentrations. Conditions in the aquifer would more likely buffer the decline in pH, lowering Fe II in groundwater.

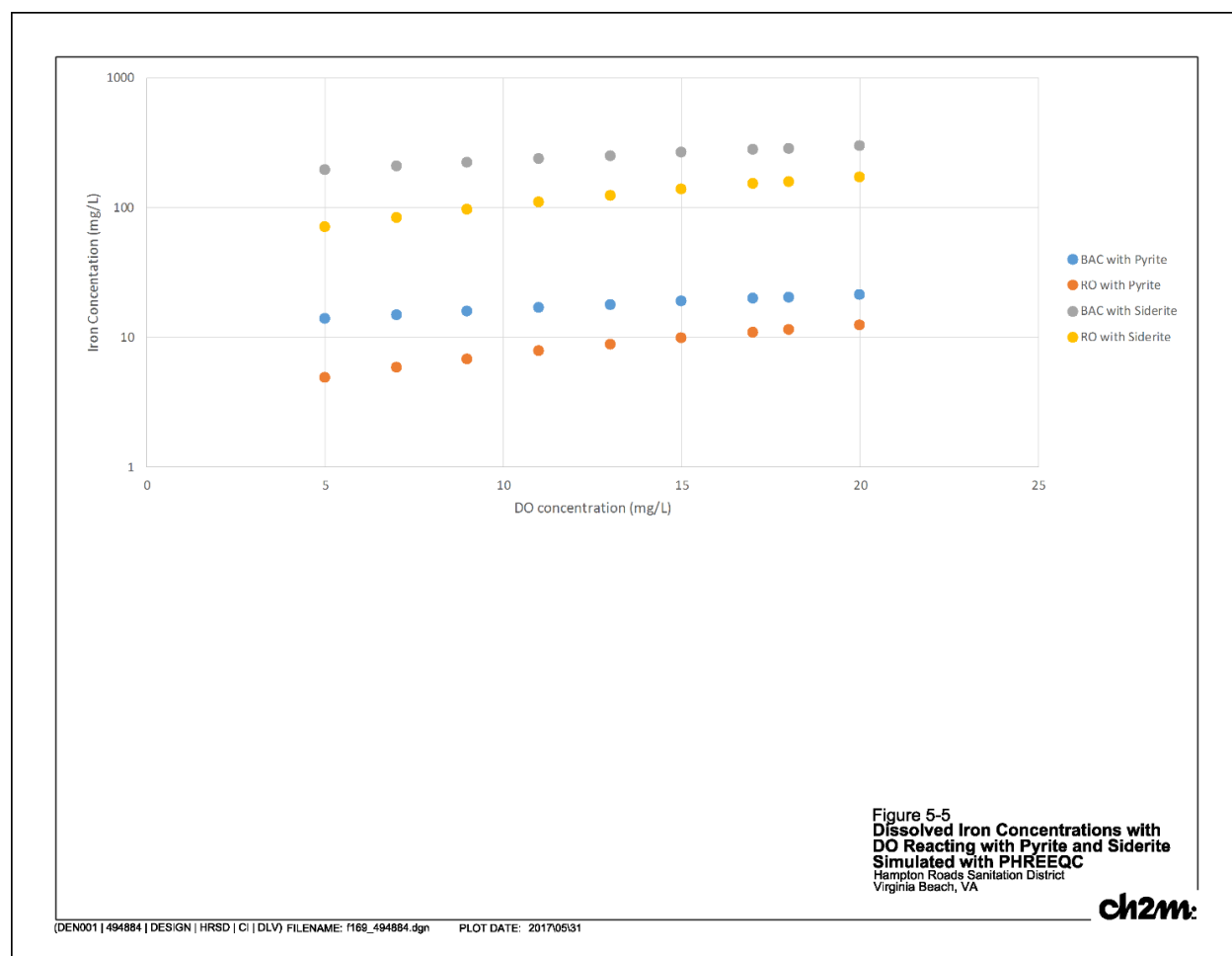


Figure 5-5. Dissolved Iron Concentrations with DO Reaction with Pyrite and Siderite
Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

5.2.2.2 Pyrite Oxidation

Similar to siderite, pyrite at a concentration of one percent abundance was reacted with recharge water containing DO concentrations ranging from 5 to 20 mg/L. Reacting membrane-based recharge water with pyrite released Fe II and the bisulfide ion (Evangelou, 1995). Upon encountering DO, Fe II oxidized to the ferric (Fe III) ion which also acts as a strong oxidant, continuing the oxidation of pyrite (Figure 5-5). Fe III eventually precipitates as HFO, lowering the pH of the surrounding pore water. The

bisulfide ion (S_2) further reacts with DO to form sulfuric acid (H_2SO_4), also lowering the pH of the surrounding pore water.

Modeling results showed that Fe II concentrations increased from 4.9 to over 21 mg/L at DO concentrations of 5 to 20 mg/L, respectively. The pH declined to 6.9 during the simulations between pyrite and carbon-based recharge water (Figure 5-6). With the low TDS concentration in membrane-based recharge water, the recharge contains little capacity to buffer reactions that precipitate HFO, while creating sulfuric acid.

Accordingly, the pH of membrane-based recharge water after reacting with pyrite dropped below 4.0. At a DO concentration of 5 mg/L expected for membrane-based recharge water, the pH declined to 3.9.

The modeling does not account for the affinity of interstitial clay minerals for adsorbing or exchanging H^+ ions, a potential buffering mechanism for acid production during pyrite oxidation.

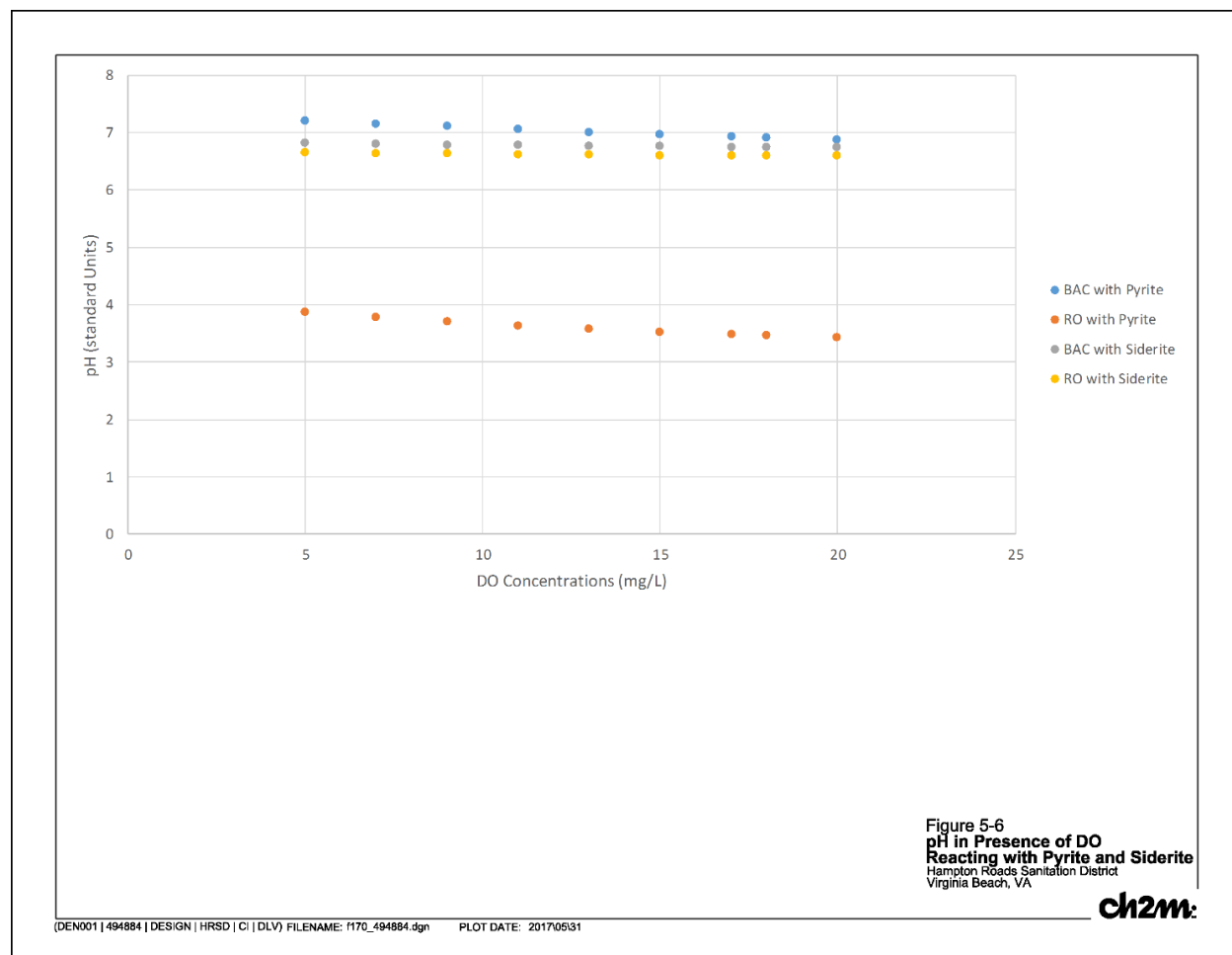
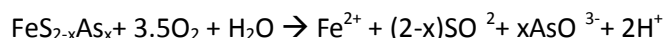


Figure 5-6. pH in Presence of DO Reacting with Pyrite and Siderite
Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

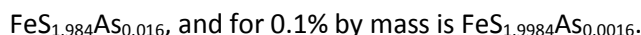
5.2.2.3 Arsenic Mobilization Effect

Pyrite can also contain manganese and cadmium, substituting for Fe II in the atomic structure of the mineral. By comparison, arsenic substitutes for sulfur in pyrite as arsenic (As) III. The overall reaction for oxidizing arsenical pyrite with molecular oxygen equals:



As III is first liberated from pyrite and then oxidizes to As V in most groundwater environments. However, depending on the environment, kinetics may control the rate of reaction for converting As III to As V.

Studies on the composition of pyrite have shown a wide range of arsenic substitution (Jones, et al, 2007; Kolker and Nordstrom, 2001). In cores from Florida, x-ray fluorescence analysis indicated that arsenic substituted for sulfur in 10 percent of the available sites. However, other studies revealed significantly lower amounts of substitution, ranging between 0.1 and 1% by mass of total pyrite. The formula for pyrite with 1% by mass of arsenic equals:



The release of arsenic from pyrite was simulated with PHREEQC. As a substitution for sulfur, arsenic concentrations were estimated as 1 percent by weight of the mass of pyrite. Similar to previous simulations one mole of pyrite was equilibrated with membrane-based and carbon-based recharge waters containing DO concentrations ranging from 5 to 20 mg/L. Applying this approach, arsenic concentrations increased from 17 to nearly 140 ug/L in reactions with membrane-based and carbon-based recharge waters, at DO concentrations ranging from 5 to 20 mg/L.

5.2.3 Identification of Impacts Related to Dissolution and Precipitation

Based on the evaluation of mineral dissolution and precipitation reactions above the following impacts have been identified (Table 5-8):

Table 5-8. Identification of Impacts due to Mineral Dissolution and Precipitation

Geochemical interaction	Identified Potential Impact	Cause	Effect
Recharge Water/Groundwater Mix with Aquifer Matrix	No identified impact	NA	NA
Recharge Water with Aquifer Matrix	Iron mobilization	DO in recharge water oxidizes pyrite, dissolves siderite, lowers pH and releases iron	Water quality impacts/aquifer degradation
	Arsenic mobilization	DO in recharge water oxidizes pyrite, lowers pH and releases arsenic	Water quality impacts/aquifer degradation
	Lowering of pH	Oxidation reactions form acidic byproducts	Further mobilization of metal bearing minerals and destruction of HFO passivation coatings

Note:

NA = not applicable

5.2.4 Mitigation Approaches for Mineral Dissolution and Precipitation Impacts

The modeling of the recharge water with the aquifer matrix indicates the potential for mineral dissolution of siderite and pyrite to release significant quantities of iron, and pyrite dissolution that has the potential to release arsenic if present. Even though EDX showed no evidence of arsenic in formation samples, conservative analysis requires considering that arsenic is present somewhere in the aquifer. Considering the potential for arsenic occurring in reactive minerals like pyrite, recharge water adjustments can be made to prevent the mobilization of the constituent.

5.2.4.1 Mitigating Pyrite Oxidation and Siderite Dissolution (Iron Mobilization)

At other injection-type facilities recharging aquifers beneath the Atlantic Coastal Plain like aquifer storage and recovery (ASR) wells, siderite and pyrite dissolution is addressed by increasing the pH of the recharge by adding sodium or potassium hydroxide. Increasing the pH raises the recharge water pH above the solubility limit of iron, diminishing the dissolution of iron-bearing minerals. Increasing the pH will lower Fe (III) solubility while increasing the rate of iron oxidation ($\text{Fe (II)} \rightarrow \text{Fe (III)}$).

Moreover, sufficient alkalinity allows HFO precipitation on the surface of pyrite and siderite, thus, passivating the minerals to future reactions in the aquifer environment. Furthermore, an alkaline pH prevents dissolution of siderite. In addition to isolating the minerals, HFO surfaces display excellent adsorption properties, adsorbing metals migrating in the aquifer environment including arsenic and Fe II (Figure 5-7). Iron adsorbs as a surface precipitate on HFO, while these surfaces exhibit an affinity for adsorbing arsenic at the pH values encountered in groundwater environments (Dzomback and Morel, 1990). Methods involving the conditioning of siderite appear in a subsequent section.

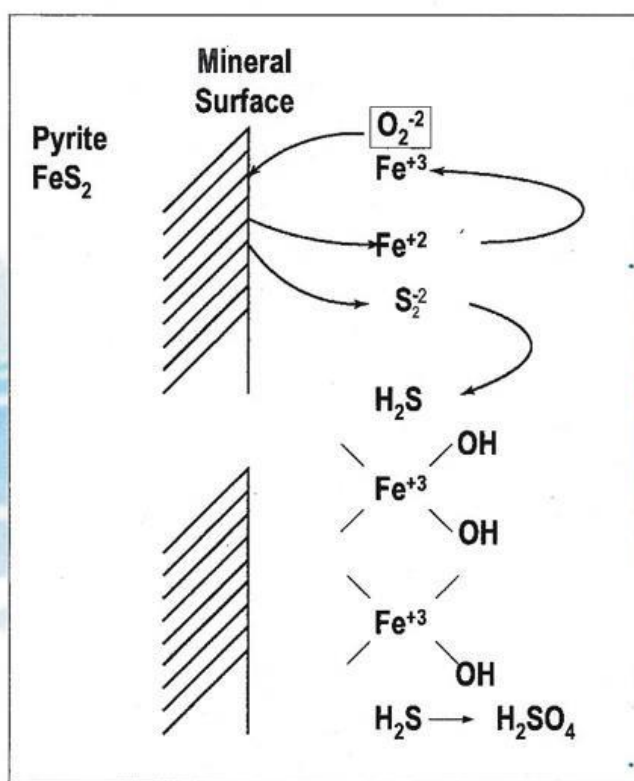


Figure 5-7. Conceptual Depiction of Pyrite Oxidation

Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

PHREEQC was used to simulate adjusting the pH of membrane-based recharge water and carbon-based recharge water containing DO from 7.0 to 8.0 in the presence of pyrite. Fe II concentrations approaching 10 mg/L during reactions with only DO, fell to less than 1.0×10^{-8} mg/L in simulations with recharge pH adjusted up to 8.0. Fe II was nearly completely oxidized to Fe III which precipitated as Fe(OH)_3 . The modeling results illustrate how well adjusting the pH of the recharge can control Fe II concentrations.

5.2.4.2 Mitigating Pyrite Oxidation (Arsenic Mobilization)

Similar to relationships between pyrite and iron, arsenic concentrations simulated with PHREEQC, represent conservative conditions. HFO surfaces in aquifer settings display a strong affinity for adsorbing the oxyanions of arsenic, comprising arsenite (As III) and arsenate (As V), and lowering its concentrations in groundwater. The program PHREEPLOT (Kinniburgh, 2011) was applied to assess the equilibrium of arsenic and its relationship with HFO surfaces (Figure 5-8). PHREEPLOT combines PHREEQC with a group of plotting programs. The phase diagram developed using PHREEPLOT shows that the recharge and native groundwater chemistries fall in arsenate fields (As V). The As V fields included AsO_4^{3-} and NaAsO_4^{2-} . Equilibrium relationships portrayed in the diagram suggest that if pyrite releases As III, it should oxidize to As V. The plot also implies that HFO appears in equilibrium with these oxy-anions. The relationship suggests that developing HFO surfaces should adsorb arsenic if released in the PAS. Additionally, the kinetics of oxidizing As III to As V appear relatively slow in groundwater environments with only DO controlling the oxidation process (Smedley and Kinniburgh, 2001).

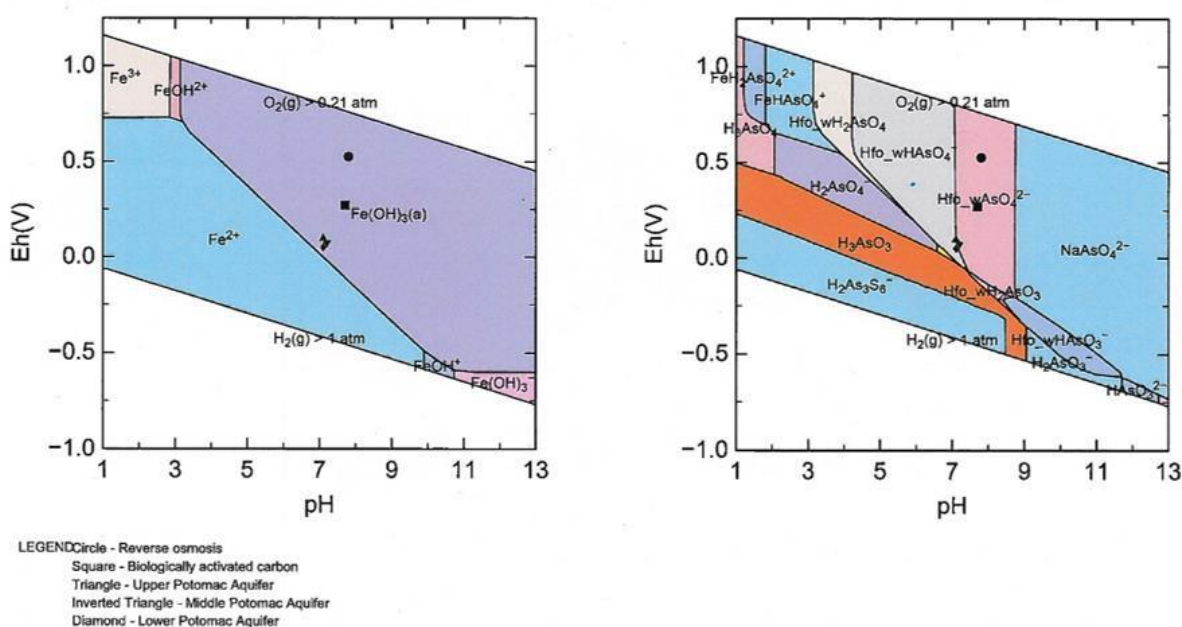


Figure 5-8. PHREEPLOT Diagram Showing Arsenic and Iron Equilibrium

Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

5.2.4.3 Aquifer Matrix Passivation and Precipitation Management (pH and Buffering Alkalinity)

To mitigate potential pyrite oxidation or siderite dissolution caused by reactions when DO in the recharge contacts these minerals in the PAS, the pH of carbon-based recharge water should be increased by the addition of sodium hydroxide (NaOH). The following factors need to consider when adjusting the pH:

- The addition of NaOH should provide sufficient amounts of hydroxyl ion to precipitate HFO to reduce the reactivity of these minerals while developing the adsorptive surfaces to prevent migration of undesirable metals in the aquifer.
- The recharge should contain sufficient buffering alkalinity to maintain the pH in the aquifer to protect HFO surfaces from dissolution in the face of acid-producing reactions caused by pyrite oxidation or siderite dissolution.

- The adjusted pH must be managed to avoid the precipitation of CaCO_3 , a common clogging agent in MAR wells.

PHREEQC and WATER!PRO™ (ChemSW, 1996) were used to evaluate the relationship between recharge pH, alkalinity, NaOH dosage (at 100% solution strength) the Langlier Saturation Index (LSI), the SI of calcite (CaCO_3) and its isomorphs, and the SI of HFO surfaces (Table 5-9). Typically, an SI greater than +0.3 or less than -0.3 indicates that mineral will precipitate or dissolve, respectively. Although at pH values of 7.0, HFO appears safe from dissolution, below 7, the SI of HFO progressively decreases towards under-saturation (6.9 - -0.07; 6.8 - -0.19; 6.7 - -0.31) at only mildly lower pH. The modeling results suggest that maintaining a pH greater than 6.7 in the aquifer will prevent the dissolution of carefully developed HFO surfaces. Similarly, to prevent precipitating CaCO_3 in the recharge, LSI and SI values should not exceed +0.3. Accordingly, the recharge pH should not exceed 7.8.

Table 5-9. Summary of Modeling Results on Carbon-based Recharge Before and After Adding Calcium Chloride

pH (standard units)	SI CaCO_3	LSI ²	Alkalinity mg/L	Caustic Dosage ³ mg/L	SI Amorphous $\text{Fe}(\text{OH})_3(\text{a})$ (HFO)	SI CaCO_3 after adding 50 mg/L CaCl_2	LSI after adding 50 mg/L CaCl_2
7	-0.61	0.64	110	0	0.1	-0.33	-0.35
7.1	-0.57	0.53	114	3	0.27	-0.22	-0.24
7.2	-0.42	0.41	118	6	0.37	-0.11	-0.11
7.3	-0.36	0.31	120	8	0.47	0	-0.01
7.4	-0.22	0.18	123	10	0.57	0.1	0.11
7.5	-0.06	0.11	124	11	0.67	0.2	0.18
7.6	0.05	0.02	126	12.5	0.77	0.31	0.31
7.7	0.15	0.12	127	13.5	0.86	0.41	0.41
7.8	0.25	0.24	128	14.5	0.94	0.51	0.52
7.9	0.35	0.31	129	15	1.04	0.61	0.59
8	0.45	0.41	130	15.7	1.11	0.71	0.69

Notes:

¹ SI = Saturation index

² LSI = Langlier saturation index

³ Dosage of NaOH at 100% strength solution

CaCl_2 = calcium chloride

PHREEQC was also applied in determining the minimal alkalinity concentrations for buffering the pH of stored water after reactions between recharge containing variable amounts of DO and an aquifer matrix composed of reactive iron bearing minerals. As shown by the modeled SI values for HFO, alkalinity concentrations in the recharge should provide sufficient buffering to maintain a pH of 6.7 in the aquifer to protect HFO surfaces from dissolution (Figure 5-9).

In this set of simulations, the iron sulfide mineral, pyrite was equilibrated with our expected recharge chemistry comprising a pH of 7.8, and DO varying between 5 and 20 mg/L. As carbon-based recharge water already displays alkalinity concentrations exceeding 100 mg/L, a hypothetical simulation was conducted at 50 mg/L to demonstrate the sensitivity of the geochemical system to broader changes in alkalinity. The alkalinity was also tested at 110, 130, 150, 175, and 200 mg/L. Alkalinity was entered in the model according to the PHREEQC notation. Oxidizing pyrite with DO creates sulfuric acid, by

definition a strong acid, and so, presents a conservative situation for testing the capacity of an agent buffering the pH during reactions in a storage aquifer

Simulation results indicated that the minimum alkalinity required to maintain a pH of greater than 6.7 after reactions between pyrite and the recharge, ranged between 110 and 130 mg/L (Figure 5-9). Coincidentally, these concentrations correspond with alkalinity in carbon-based recharge water before and after adjusting the pH from 7.0 to 7.8. Thus, no additional alkalinity is required to maintain a pH of 6.7 in the PAS. Setting an even higher alkalinity could maintain the pH above 7.0, but increase chemical costs, significantly, while requiring another chemical feed. Simulations performed at other MAR sites in the Atlantic Coastal Plain where chemical addition is required to increase the alkalinity of the recharge show similar results, with an alkalinity in the recharge water of approximately 100 mg/L proving sufficient to maintain pH in the receiving aquifer.

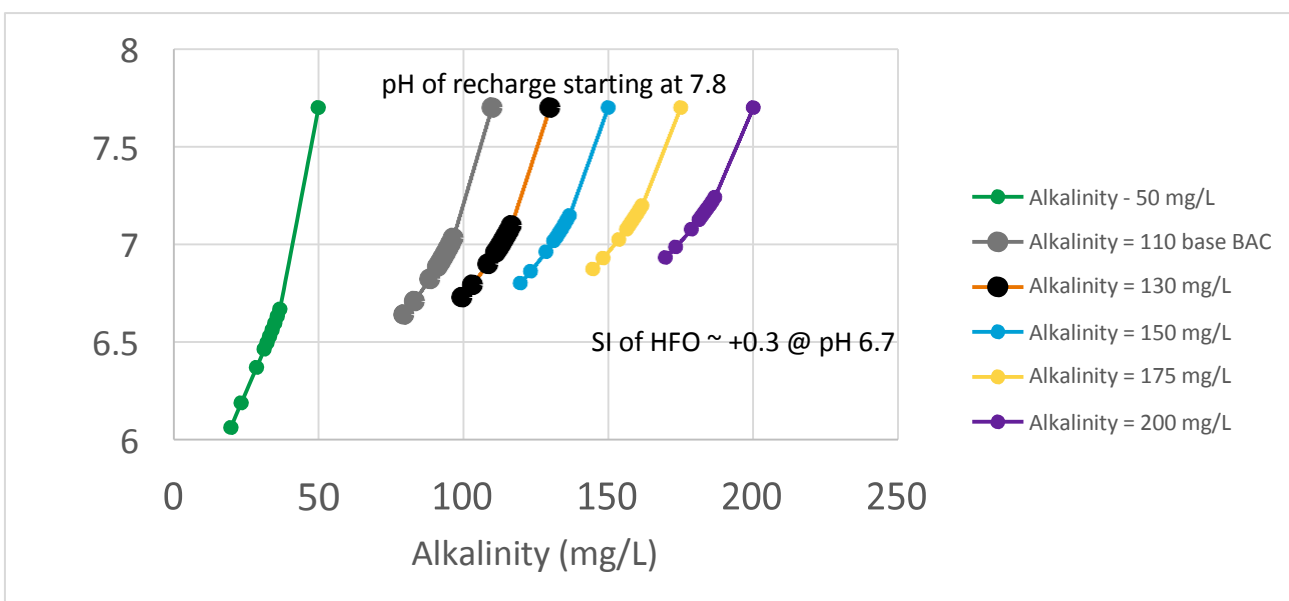


Figure 5-9. Buffering of Reactions in the PAS with Carbon-based Recharge Water of Varying Alkalinity
Evaluating the Compatibility of Recharge water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads
Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

5.3 Clay Structure Fragmentation

Damage can also arise when injectate displays differing cation chemistry than the native groundwater and the clay minerals (Langmuir, 1997). Exchanging cations can disrupt the clay mineral structure particularly when their atomic radius exceeds the radius of the exchanged cation. The larger cation fragments the tabular structure, shearing off the edges of the mineral (Figure 5-10). Plate-like fragments break off the main mineral particle and migrate with flowing groundwater. Like the damage incurred by water of differing ionic strength, migrating clay fragments will brush pile in pore spaces, physically plugging passageways and reducing aquifer permeability. Unlike the accumulation of TSS in the wellbore, formation damage by migrating clays develops in the aquifer away from the wellbore, making its removal difficult by backflushing or even invasive rehabilitation techniques.

Cation exchange describes the substitution of cations in solution for those held by a mineral grain. Cation exchange mechanisms are debated, but most agree are driven by a net negative surface charge on mineral surfaces. Samples of the confining units and clay rich aquifer sands were submitted for CEC analysis. CEC analysis involves determining the amount of a cation that a specific substance can remove once the mineral, reacting substance, and surrounding solution equilibrate.

5.3.1 Evaluation of Clay Structure Fragmentation Results

CEC results from the samples submitted from test well TW-1 indicates that the cumulative CEC ranges from 28.52 to 52.72 milli-equivalents per 100 grams (meq/100g) of sample (Table 5-10). Samples displaying the largest CEC corresponded to the confining units, which also contained the largest amounts of clay. Clay content when compared with CEC exhibited a linear relationship (Figure 5-11), that allowed projecting the CEC to samples containing lower amounts of clay, like the aquifer sands. According to the projections the cumulative CEC values in aquifer sands containing around 5 percent interstitial clay is anticipated to amount to approximately 15 meq/100g.

CEC also involves a replacement sequence depending on the specific cations present. The hierarchy of exchangeable cations proceeded as follows: calcium (Ca) > sodium (Na) > magnesium (Mg) > potassium (K). The sequence was not expected as the PAS groundwater at Nansemond displayed a strongly sodic chemistry, insinuating sodium should appear as the prevailing cation in the hierarchical sequence removed from the clays. The dominance of calcium suggests that fresher, non-sodic groundwater may have resided in the PAS, previously, leaving behind calcium in the exchange position of clay minerals.

In contrast, aquifer sand and confining bed samples collected in the UPA, MPA, and intervening clay confining bed at the City of Chesapeake's ASR well showed an authigenic, instead of detrital origin, dominated by kaolinite and illite, cumulative CECs ranging from 0.3 to 13.3 meq/100g, and an exchangeable cation hierarchy displaying a Na > Mg > K > Ca sequence, more typical of aquifer sands containing brackish or salty water.

5.3.2 Identification of Impacts Related to Clay Structure Fragmentation

Clay structural fragmentation due to cation exchange occurs when larger cations exchange with smaller cations within individual clay particle structures. The native groundwater at Nansemond is a sodium chloride type water, which matches that of the carbon-based recharge water. Given that the waters are of the same type, no cation exchange is anticipated to be a problem, even though calcium resides with sodium in the exchange sites of these clays.

5.3.3 Mitigation Approaches for Clay Structure Fragmentation Impacts

Cation exchange is not anticipated to be problematic at the Nansemond Recharge Site. However, due to the differing ionic strengths between the recharge water and native groundwater, a clay conditioning salt flush is being proposed (discussed in more detail in Sections 5.4) consisting of hydroxy-aluminum chloride solution. This salt flush will promote cation exchange within the clay particles with a higher valence cation (Al³⁺) which will tighten the bonds between the clays and promote their structural stability.

The solution creates a Al₆(OH)₆⁺ polymer, featuring a +6 charge beneficial for adsorption or cation exchange with sodium montmorillonite clays in the LPA. The charge helps bind clay particles together, makes stronger attachments to framework grains, and tightens interlayer spacing in the clay structure.

Binding particles to each other represents an important mechanism for preventing clay dispersion, probably more important than exchanging with cations in interlayers. The polymeric molecule creates an irreversible reaction, protecting interstitial clays from dispersing in the presence of fresh recharge waters.

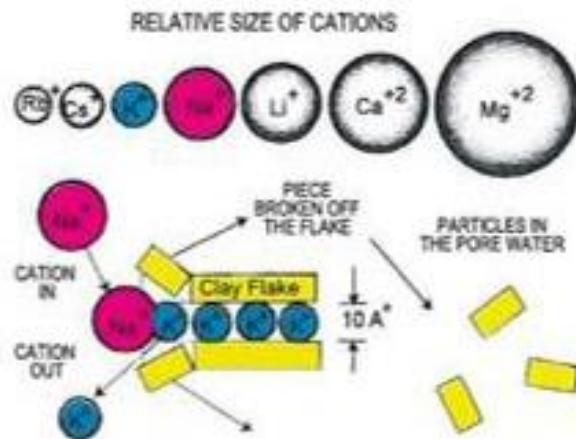


Figure 5-10. Mechanisms of Clay Particle Disaggregation and Migration During Injection Operations
Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

Table 5-10. Summary of Cation Exchange Capacity Found in Samples From TW-1

Sample No.	Depth (fbg)	Relation to Aquifer	Calcium (meq/100g)	Magnesium (meq/100g)	Sodium (meq/100g)	Potassium (meq/100g)	Cumulative CEC	Clay Content of Sample (%)	Selectivity Order
1	465 to 475	Confining bed above UPA	27.8	5.94	8.36	2.7	44.8	44.5	Ca>Na>Mg>K
2	700 to 710	Confining bed in UPA	20.2	3.22	4.53	1.17	29.12	33	Ca>Na>Mg>K
3	925 to 935	Confining bed in MPA	21.8	3.32	6.43	1.06	32.61	27.3	Ca>Na>Mg>K
4	1020 to 1030	Confining bed in MPA	25	6.88	18.3	2.54	52.72	65	Ca>Na>Mg>K
5	1145 to 1155	Confining bed between MPA and LPA	16.3	3.73	7.61	0.884	28.524	27	Ca>Na>Mg>K

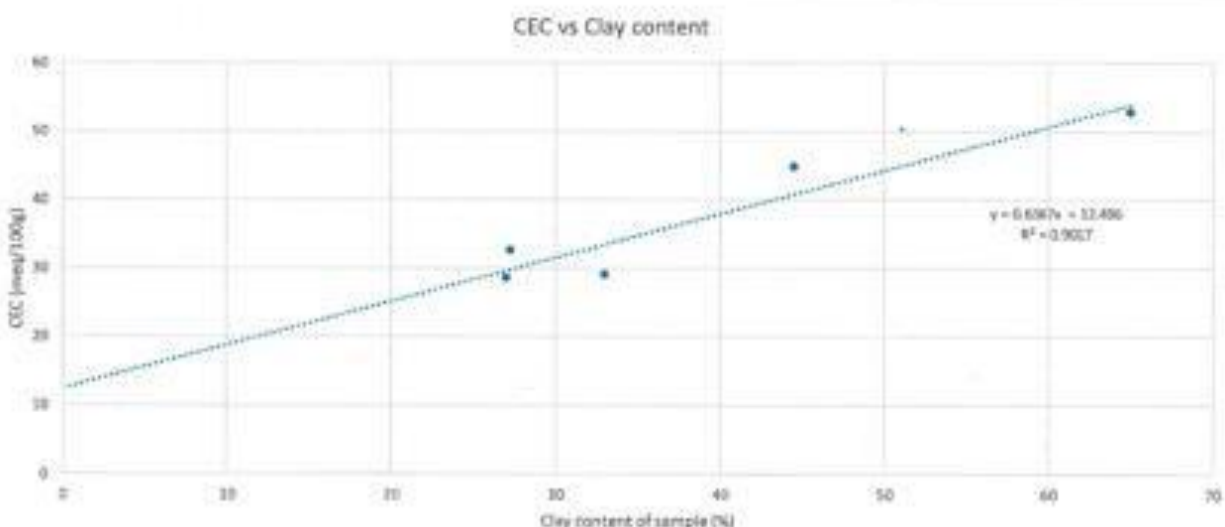


Figure 5-11. Relationship Between Clay Content and CEC

Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

5.4 Clay Particle Dispersion Evaluation

The damaging of clays occurs with the disruption of their mineral structure. The damage can arise when injecting water of significantly different ionic strength than the native groundwater, a concern when injecting dilute fresh water into an aquifer containing brackish or saline native groundwater (Drever, 1982). The dilute water contains significantly less cations, and a weaker charge than brackish native groundwater. When displacing the brackish water in the diffuse-double layer between clay particles, the weaker charge can induce repulsive forces dispersing the particles, fragmenting the clay structure while mobilizing the fragments into flowing pore water. The particles can eventually accumulate in smaller pores physically plugging the pore space, and reducing the permeability of the aquifer.

Evaluating the chemistry of the recharge water (membrane-based and carbon-based) and native groundwater from the PAS revealed the following concerns:

- Membrane-based displayed a lower ionic strength differing by greater than two orders of magnitude from the native groundwater in the UPA, MPA, and LPA whereas the ionic strength of carbon-based fell roughly within the same order of magnitude as the PAS aquifers (Figure 5-12).
- With the exception of sodium (2.9 mg/L), individual cation concentrations did not exceed 1.0 mg/L in the membrane-based sample. Given the low cation concentrations, ion exchange should not represent a significant concern for the use of membrane-based process as recharge.

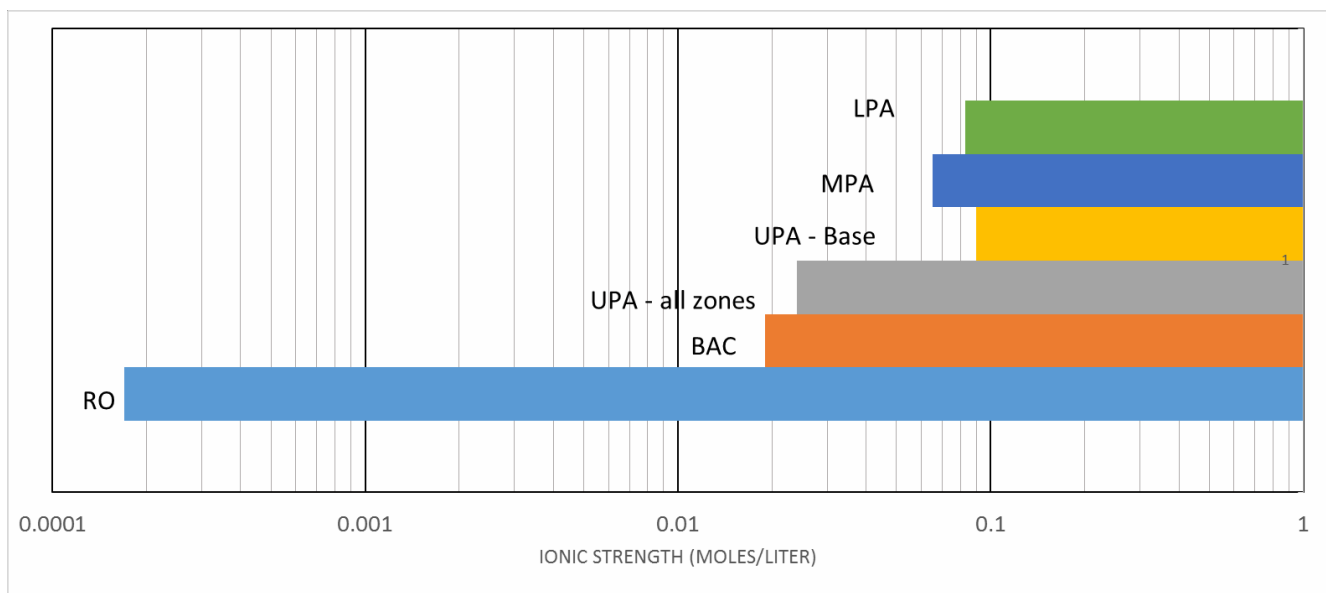


Figure 5-12. Graph Showing Varying Ionic Strengths of Recharge and Native Groundwater
Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

5.4.1 Influence of Ionic Strength

As a dilute, treated water, the ionic strength of the membrane-based recharge water appeared lower than groundwater in the three PAS aquifers by at least one order of magnitude. By comparison, the ionic strength of carbon-based recharge water, although approaching one half an order of magnitude than the native groundwater, fell within the same order of magnitude.

5.4.1.1 Ionic Structure of the Aquifer Matrix Clay Particles

One of the most important factors leading to the dispersion of clay minerals involves a change in the double layer thickness of a clay particle (Figure 5-13). A double layer of ions lies adjacent to clay mineral surfaces, or between the mineral's structural layers because a negative charge attracts cations toward the surface.

As the fluid must maintain electrical neutrality, a more diffuse layer of anions (negative charge) surrounds the cations.

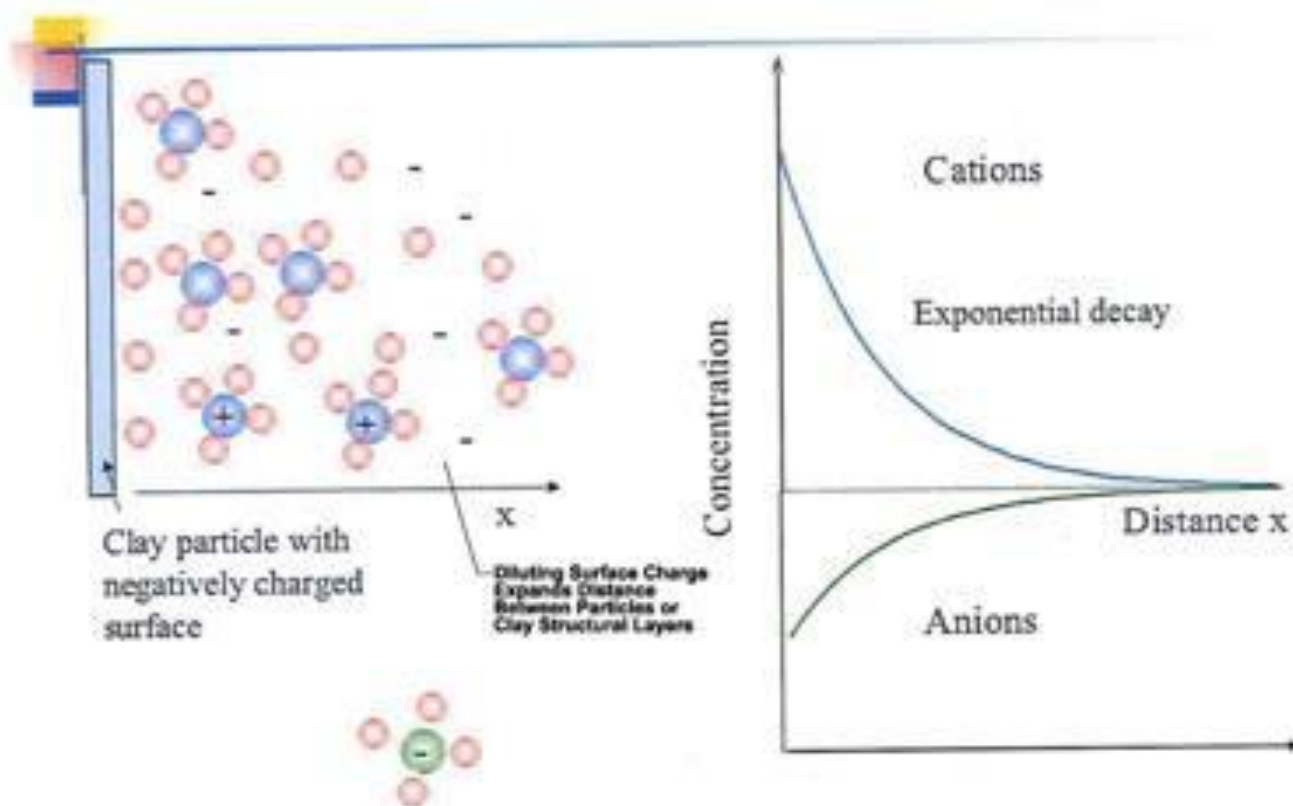


Figure 5-13. Diagram of Diffuse Double Layer in Clay Minerals

Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

5.4.1.2 Influence of the Ionic Strength of the Water on Clay Particle Structure

When the concentrations of ions are large, as in brackish water, the double layer around the particle, or situated between the clay's structure layers gets compressed to a smaller thickness by the stronger charge. Compressing the double layer causes particles to coalesce, forming larger aggregates, a process called clay flocculation. When the ionic concentration of a fluid invading the aquifer is significantly lower than the native groundwater, the charge weakens and the diffuse double layer expands, forcing clay particles and structural layers within clay minerals apart. The expansion prevents the clay particles from moving closer together and forming an aggregate (Figure 5-14).

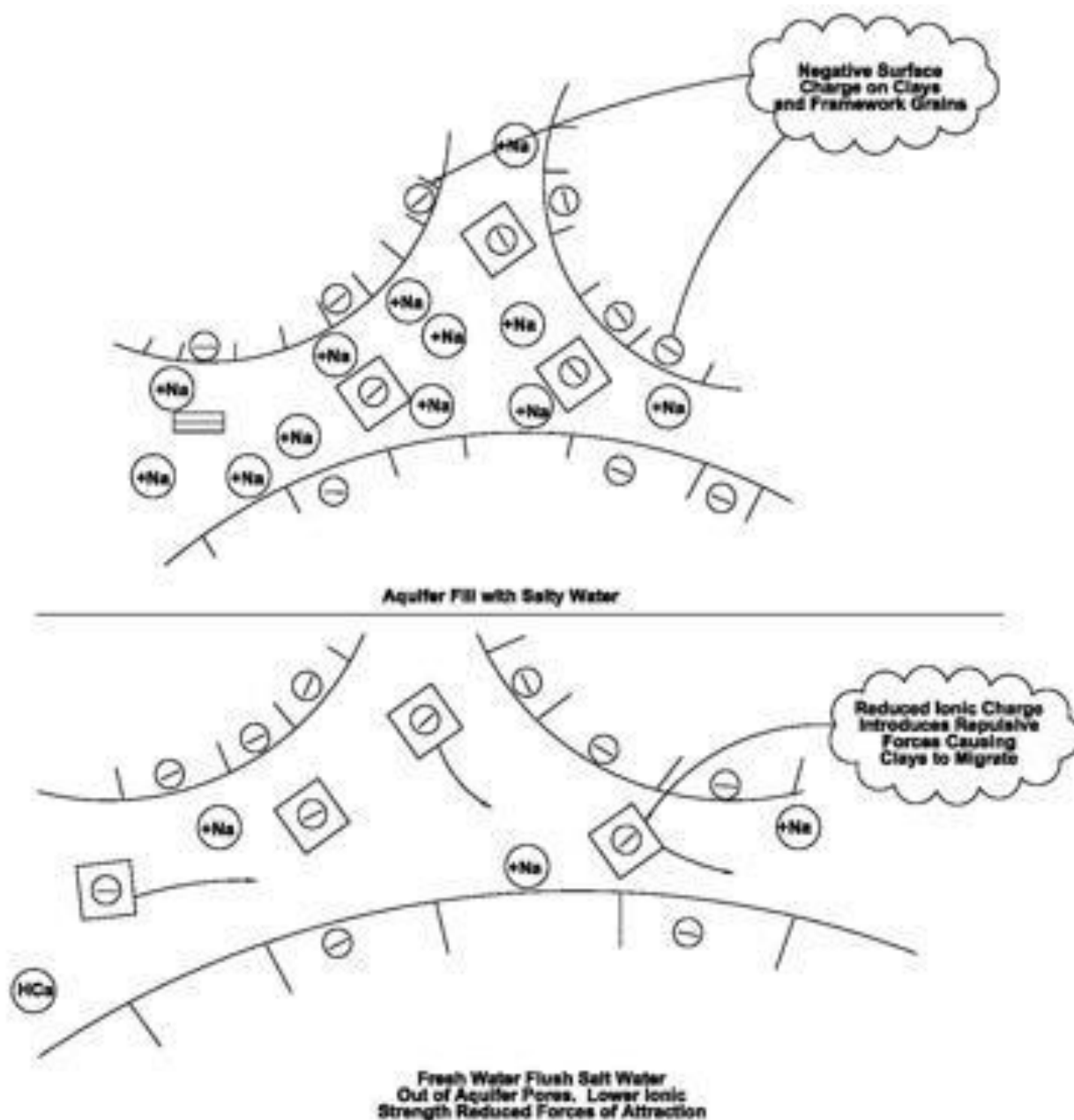


Figure 5-14. Effect of Changing Ionic Strength of Native Groundwater
*Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads
 Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1*

5.4.1.3 Impact of Changing Clay Structure

Operationally, recharging the aquifer with treated water exhibiting a significantly lower ionic strength than the native groundwater can damage interstitial clay minerals attached to aquifer framework particles, weaken inter-particle attachments, and even diminish charges between individual clay layers. All these factors cause clay minerals and mineral fragments to migrate through the pore spaces of the aquifer. The fragments eventually block pore throats, reducing the permeability of the aquifer around a MAR well, diminishing the well's injection capacity. Most literature sources (Meade, 1964; Reed, 1972; Khilar and Fogler, 1984, and Gray and Rex, 1966) cite a disparity exceeding one of order of magnitude in ionic strength can cause formation damage.

The tendency toward dispersion is measured in clay minerals by their zeta potential according to the following relationship:

$$Z = 4\pi\epsilon q/D \text{ where:}$$

ϵ = thickness of the zone of influence surrounding the charged particle Q = charge on the clay particle before attaching cations

D = dielectric constant of the liquid

For any solution and clay mineral, reducing the zeta potential involves lowering the thickness of the zone of influence. Substituting small, divalent or trivalent charged cations such as Ca^{+2} or Al^{+3} , respectively, in place of a large singly charged, hydrated ions, like Na^{+1} lowers the zeta potential, permitting clay particles to coalesce. This behavior explains the tendency for sodium to cause clay dispersion while calcium and aluminum induce its flocculation.

More important, the ionic strength of the infiltrating, fresh water like membrane-based recharge water is significantly less than the brackish water contained in the MPA, LPA, and discrete sand intervals of the UPA. The saltier water containing higher concentrations of cations and according to diffuse layer theory (Honig and Mul, 1971) providing a stronger bond between clay minerals and aquifer framework minerals like quartz. The weaker bond inherent with membrane-based recharge water can create repulsive forces that loosen the clays from framework grains.

5.4.1.4 Summary of Impact of Ionic Strength of Recharge Water

The low ionic strength of membrane-based recharge water in comparison to the PAS groundwater represents a concern for injection operations, particularly for its potential to disperse clay minerals. Clay dispersion describes an electro kinetic process (Meade, 1964; Reed, 1972; and Gray and Rex, 1966), where an electrostatic attraction between negatively charged clay particles is opposed by the tendency of ions to diffuse uniformly throughout an aqueous solution. Therefore, recharge water, from either the membrane-based or carbon-based treatment processes, will cause plugging of the well and aquifer without some conditioning approach to aquifer recharge.

5.4.1.5 Regional Anecdotal Example

An ASR facility tested by USGS in the 1970s at Norfolk, Virginia exhibited greater than 80 percent reduction in injectivity after only 150 minutes of starting injection operations (Brown and Silvey, 1977). The ASR well was installed in the UPA, screening nearly 85 feet of sand in the unit. Groundwater from the UPA displayed a TDS concentration around 3,000 mg/L, while recharge provided by the City of Norfolk exhibited concentrations around 100 mg/L. The USGS employed nuclear, electrical, and mechanical geophysical logging techniques to evaluate the origin of the injectivity losses and discriminate between the causes of clogging documented at other sites, like TSS loading.

Injectivity losses caused by clogging from TSS loading typically occurs at discrete zones through the well screen. In contrast, geophysical logging of the ASR test well at Norfolk showed hydraulic conductivity losses distributed evenly across the entire screen. Also, in comparison to clogging by TSS which responds positively to mechanical and chemical rehabilitations, the USGS was able to restore only a fraction of the well's original injectivity.

To arrest the declining injectivity, the USGS treated the wellbore and proximal aquifer with a concentrated calcium chloride ($\text{CaCl}_2 > 1,000 \text{ mg/L}$) solution. As described above, the doubly charged, calcium cation forms a stronger particle and inter-layer bond than the monovalent cation, sodium. Using a concentrated solution ensures calcium exchanges for sodium at the maximum number of sites. After applying the treatment at Norfolk, the injectivity of the ASR test well remained stable (yet low) over two more test cycles, before the project was ended.

5.4.2 Candidate Mitigation Approaches for Clay Dispersion

As concluded in previous sections, the recharge water must be conditioned in some manner to avoid disrupting the clay particles in the aquifer and causing plugging of the well/aquifer. The approach to stabilizing the aquifer involves changing clay mineral suites by applying divalent and trivalent cation salts to stabilize clay minerals. Therefore, different aquifer pre-conditioning schemes will be evaluated for how well they stabilize the clay minerals, through preventing the repulsion of the clay particles and subsequent clogging of the aquifer pore spaces.

Modeling was conducted to simulate the following measures used in stabilizing clay minerals in the PAS:

- Treating the LPA with a calcium chloride flush
- Treating the LPA with an aluminum chloride flush
- Adding 50 mg/L of calcium chloride to carbon-based recharge

CEC for calcium, magnesium, potassium, and sodium obtained from the mineralogical analysis of aquifer sands was applied in developing input to modeling for conditioning clays in the LPA with a calcium salt flush. In this testing, the LPA was recognized as exhibiting the greatest concentrations of chloride and TDS, thus, presenting the greatest risk for clay dispersion during injection operations.

5.4.2.1 Treating the LPA with a Calcium Salt Flush

CaCl₂ and aluminum chloride (AlCl₃) flushes involve mixing a concentrated solution to ensure exchange in the interstitial aquifer clays with the target cation (Ca⁺² or Al⁺³) contained in the treatment solution.

In aquifers 100 feet thick, 100,000 to 200,000 gallons of solution is injected into the aquifer followed by several thousand gallons of water to displace the treatment solution away from the wellbore. To prevent disrupting clays and having them flocculate in aquifer pores, the treatment is added slowly at rates less than 100 gallons per minute. Because test well TW-1, spans the three PAS aquifers, a drilling contractor will employ a packer to isolate each aquifer for treatment. The leading edge of the solution volume will extend roughly 12 to 18 feet away from the injection well, treating the area of the aquifer most sensitive (wellbore) to migrating clays.

Breeuwsma, et al. (1986) developed a technique for determining the amount of exchanger (-X) from the CEC of a cation according to the following equation:

$$X = \text{CEC} / ((100/\text{sw}) \times (\phi/1-\phi)) = \text{CEC} / (100 \times (\phi/\rho_B)) \text{ where: } X = \text{amount of exchanger (dimensionless)}$$

CEC = cation exchange capacity (meq/100g) Sw = dry weight of soil (kilograms per liter [kg/L] of soil)

ρ_B = bulk density of soil (kg/L)

ϕ = porosity of sediment (fraction)

The technique allowed entering the proportional amounts of exchanger into PHREEQC based on the actual CECs from formation samples, determined by the laboratory testing. PHREEQC was employed for evaluating the stability of clays contained in the CaO-Al₂O₃-SiO₂-H₂O and NaO-Al₂O₃-SiO₂-H₂O mineral systems (Figures 5-15 and 5-16) for the native groundwater chemistry and then after adding varying dosages of calcium chloride including 7,000, 70,000, and 700,000 mg/L.

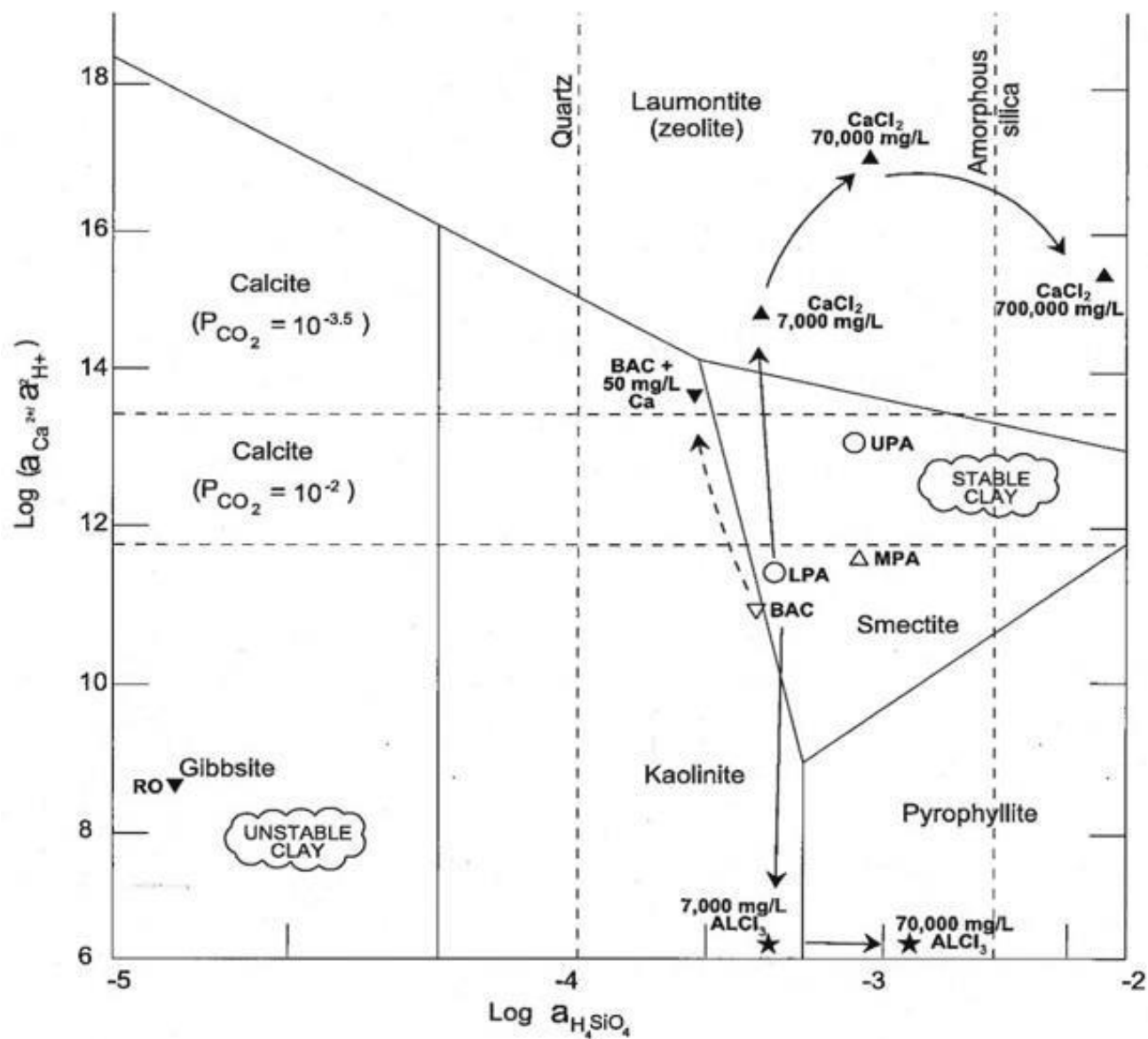


Figure 5-15. Stability Relationships among Minerals in the System $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ at 25°C
Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

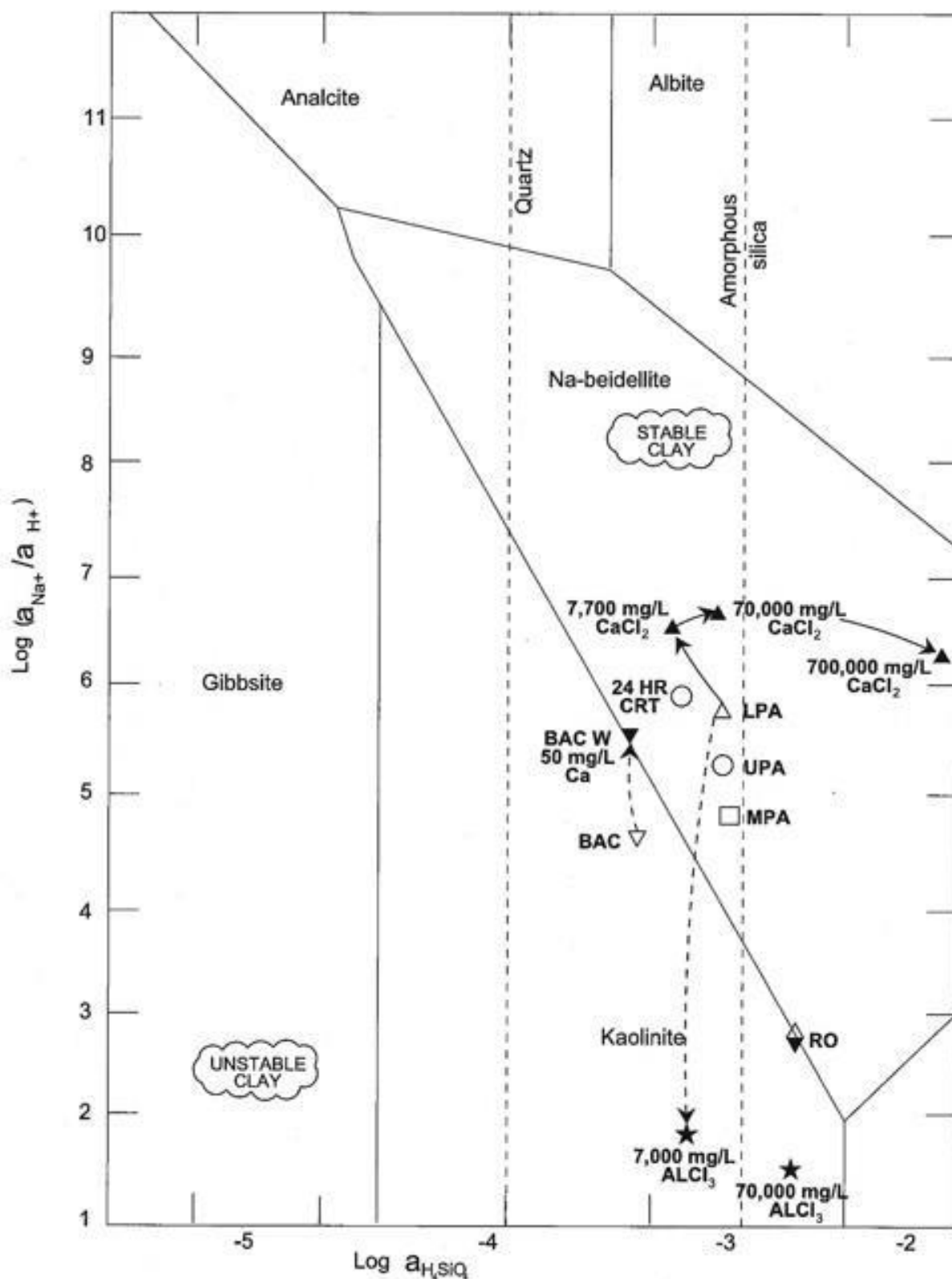


Figure 5-16. Stability Relationships among Minerals in the System $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 25°C
Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

Minerals contained in these systems represent clays and their weathering products (gibbsite, kaolinite) commonly found in sediments of the PAS. The objective of these simulations involved determining

where water quality fell into the stability fields of clay minerals, while identifying potential instabilities. The calcium chloride dosages spanned the range typically applied to treating aquifers (Brown and Silvey, 1977) for aquifers containing unstable clays in preventing the dispersion of clay minerals (Khilar and Fogler, 1984).

To prevent a significant drop in the pH of the treatment fluid, during the simulations the pH was fixed at 8.2 using potassium hydroxide.

Unlike damaging clay minerals by injecting waters of incompatible ionic strength or differing cations, precipitating clay minerals represents a relatively minimal concern for permeability loss during injection operations in the PAS. Kinetically, the precipitation of clay minerals requires significant amounts of time typically measured on a geologic time scale, rather than the service life of an injection facility.

In the $\text{CaO}^-\text{Al}_2\text{O}_3\text{SiO}_2\text{H}_2\text{O}$ system, native groundwater from the UPA fell in the upper smectite field while groundwater from the MPA and LPA plotted in the middle of the field (Figure 5-15). On the same diagram membrane-based plotted in the Gibbsite field suggesting clay instability, while carbon-based plotted in the Kaolinite field next to Smectite. Gibbsite represents a common product of deteriorating clays.

Adding solutions containing 7,000, 70,000, and 700,000 mg/L CaCl_2 to the LPA showed increasing clay stability for both concentrations. In the $\text{NaO}^-\text{Al}_2\text{O}_3\text{SiO}_2\text{H}_2\text{O}$ system, RO and BAC plotted in the Kaolinite field adjacent to Sodium-Beidellite, a sodium-aluminum silicate member of the Smectite group. Groundwater samples from all three aquifers plotted in the Sodium-Beidellite field. Similar to the $\text{CaO}^-\text{Al}_2\text{O}_3\text{SiO}_2\text{H}_2\text{O}$ system, dosing CaCl_2 slightly improved the clay mineral stability when applying the two lower dosages.

5.4.2.2 Treating the LPA with an Aluminum Chloride Flush

Like applying a calcium salt flush, aluminum salt offers benefits for stabilizing clay minerals in the PAS.

The tri-valent aluminum ion forms a strong bond in the exchange position of clays. PHREEQC was employed to simulate an aluminum chloride (AlCl_3) flush in the LPA. Unfortunately, the CEC for aluminum was not obtained for the PAS samples. The amount of exchanger calculated for calcium from the previous simulation and the two lower dosages (7,000 and 70,000 mg/L) were applied to simulating the AlCl_3 flush.

Similar to the calcium flush, increasing dosages of AlCl_3 produced migration to the right across the kaolinite field in the, $\text{CaO}^-\text{Al}_2\text{O}_3\text{SiO}_2\text{H}_2\text{O}$ and $\text{NaO}^-\text{Al}_2\text{O}_3\text{SiO}_2\text{H}_2\text{O}$ systems (Figures 5-15 and 5-16), describing increasing clay mineral stability. The small hydrated atomic radius of the aluminum ion fits easily into the inter-lattice spaces of more complex clay minerals, like montmorillonite (Figure 5-17). Considering the small aluminum radius, future testing will involve analyzing for aluminum species, an important consideration for developing the desired hydroxy-aluminum molecule without increasing turbidity of the water used for conditioning clays.

Treatments employing either calcium or aluminum chloride appear to stabilize common clay minerals in the $\text{CaO}^-\text{Al}_2\text{O}_3\text{SiO}_2\text{H}_2\text{O}$ and $\text{NaO}^-\text{Al}_2\text{O}_3\text{SiO}_2\text{H}_2\text{O}$ systems in situ. However, stabilizing clay minerals through cation ion exchange fails to portray all the benefits of the salt flushes. Employing a hydroxyl-aluminum chloride flush in results in a $\text{Al}_6(\text{OH})_{12}^{6+}$ polyelectrolyte, featuring a 6 charge beneficial for adsorption or cation exchange with sodium montmorillonite clays in the LPA. The adsorption component may prove more effective than cation exchange for connecting clay particles, strengthening attachments between clays and framework grains, and tightening inter-layer space. A discussion of the benefits and application of these treatments appears in a subsequent section.

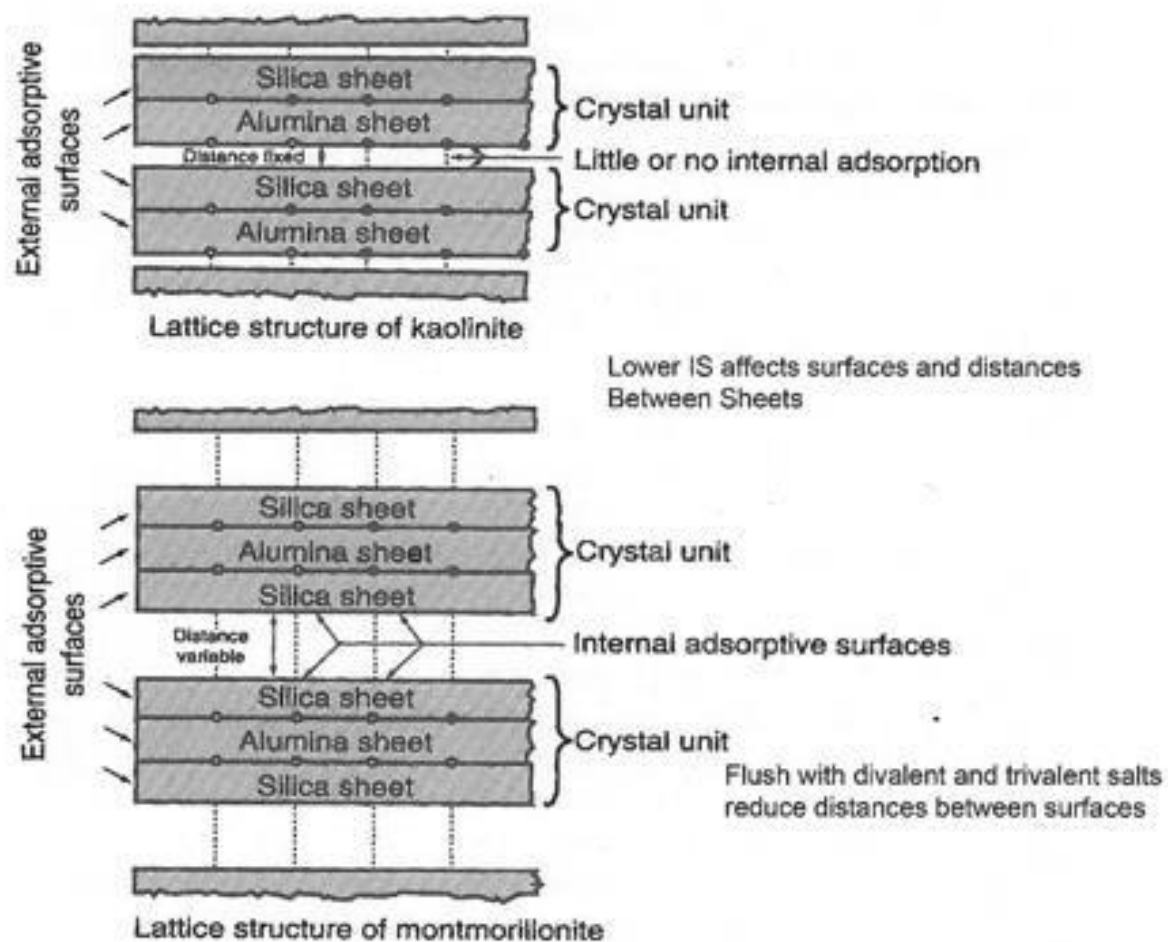


Figure 5-17. Effects of Di-/Trivalent Treatments on Clay Mineral Structure
Evaluating the Compatibility of Recharge Water, Native Groundwater, and Aquifer Mineralogy at the Hampton Roads Sanitation District's Nansemond Wastewater Treatment Plant, Test Well 1

Future Framework Implementation

The following discusses measures required to ensure that the recharge chemistry when mixed with native groundwater or reacting with aquifer minerals does not compromise injection operations by damaging the permeability of the receiving aquifer, or create environmental issues by releasing undesirable constituents.

6.1 Summary of Mitigation Approach

Table 6-1 presents a summary of the mitigation approach.

Table 6-1. Summary of Mitigation Approach

Mitigation Issue	Mitigating Action	Mitigating Objective	Summary Description
<i>Recharge Water/Aquifer Interaction</i>			
Mineral dissolution/precipitation	Adjust pH with NaOH	Prevent mobilization of iron and arsenic,	Form and maintain HFO coating Maintain pH to counter acid formation due to iron oxidation effects
<i>Aquifer Clay Matrix Stability</i>			
Clay Particle dispersion and clay structure fragmentation	Conditioning salt flush using AlCl_3	Prevent dispersion and disruption of clay particles and prevent clogging of the aquifer	Tighten the bonds between clay particles Tighten the bonds within the clay structures

6.2 Selecting the Recharge

The evaluation performed by applying conventional geochemical analysis and thermodynamic equilibrium modeling suggest carbon-based recharge water offers better characteristics as recharge than membrane-based recharge water. The ionic strength of carbon-based recharge water fell within the same order of magnitude of even the saltiest interval encountered in the PAS, during packer testing. Further, carbon-based recharge water displayed good buffering capacity should DO react with sulfide minerals in the PAS to create acid. By comparison, the ionic strength of membrane-based recharge water fell greater than two orders of magnitude below even the freshest groundwater sampled in the PAS at test well TW-1.

Montmorillonite, the clay mineral most sensitive to changes in ionic strength and cation exchange (Konikow, et. al, 2001) represented the most prevalent clay encountered in aquifer sands and confining units in the PAS. Applied as recharge without modification, membrane-based recharge water would cause significant dispersion of montmorillonite contained in the aquifer sands of the PAS.

Moreover, with no buffer capacity, reactions between DO in the recharge and pyrite, if present in the PAS, could cause a severe drop in pH of the stored water below the SMCL. As pyrite was not found during lithologic logging or microscopic analysis by a mineralogical lab, these reactions would occur locally to discrete portions of aquifer sands occupied by pyrite and thus, might not influence water quality over a measurable section of the PAS.

Making membrane-based recharge water compatible with native groundwater (and clays) in the PAS will require significantly increasing its ionic strength. As a factor of safety for initial injection operations, HRSD should increase the ionic strength of membrane-based recharge water to within roughly one-half order of magnitude of the saltiest interval found in the PAS ($9.0E-2$). This measure will involve adding sodium and chloride concentrations by 1,000 mg/L using a salt solution, increasing the ionic strength to roughly $4.0E-2$. Adding calcium ions (40 to 80 mg/L) to roughly match calcium concentrations in the native groundwater in the PAS will improve the compatibility of membrane-based recharge water with the PAS.

Increasing the buffer capacity of RO should involve adding a liquid product like sodium carbonate, sodium hydroxide, with aeration. Lime, the simplest and cheapest alternative for adding alkalinity creates significant amounts of residual solids in the recharge that will rapidly clog an injection well.

6.3 Aquifer Conditioning for Clays

Regardless of selecting either carbon-based or membrane-based treatment as the preferred recharge, HRSD should condition interstitial clay minerals in the PAS around test TW-1 and each new MAR wellbore.

As described previously, the process will involve injecting several hundred thousand gallons of a 0.1 M salt solution, containing CaCl_2 or hydroxy-aluminum chloride, storing the solution in the aquifer for several weeks, and then removing the spent solution, or driving it deeper into the aquifer by starting injection operations. The solution should treat interstitial clay minerals lying within 10 to 20 feet of the wellbore.

In aquifers prone to unstable clay minerals and turbidity in the water produced from supply wells, treatments with a concentrated salt solution often comprise a routine element of developing a new supply well. HRSD should incorporate the treatments into the development regime of all the new injection wells at the Nansemond WWTP, and potentially other locations.

Using a trivalent cation flush with hydroxyl-aluminum chloride should prove a more effective treatment than the divalent calcium chloride. The affinity of a clay for a cation usually depends upon valence:



Accordingly, the preferential exchange hierarchy for common tri-, di-, and monovalent cations comprises:



As calcium appeared as the prevailing cation in the exchange position during CEC testing, a calcium chloride flush may not achieve the same effectiveness as an aluminum chloride flush.

Because of its extended screen, spanning the three PAS aquifers, applying a treatment solution in TW-1 will require, isolating each aquifer when applying the treatment. Given that the solution is stored for one to two weeks following application, treating the three PAS aquifer units screened by TW-1 will require 6 to 8 weeks to complete. No recharge from the new Demonstration Plant should enter TW-1 before treating each aquifer interval. In addition to treating clay minerals around the wellbore, adding divalent ions like calcium during injection helps maintain the treated area (Khilar and Fogler, 1984). Adding 50 mg/L CaCl_2 to carbon-based recharge water during PHREEQC simulations shifted the water chemistry toward a more stable calcium-smectite.

For the SWIFT Research Center (SWIFTRC), it was decided to first pilot test the LPA using a hydroxyl-aluminum chloride flush and apply the learning from that investigation to TW1. It is anticipated at this time that CaCl_2 injection will not be required, but this assumption may be adjusted using an adaptive

management approach following the pilot testing program described below and pressure accumulation at the TW1 wellhead after injection is initiated.

6.3.1 Pilot Testing an Aluminum Chloride Flush

At the Demonstration Facility, HRSD will install monitoring wells that individually screen the UPA (MW-UPA), MPA (MW-MPA), and LPA (MW-LPA). These wells will consist of a 6-inch diameter casing and screen assembly. Screen intervals will span each aquifer sand encountered in test well TW-1. To test the effectiveness of an aluminum chloride flush and develop protocols before treating test well TW-1, HRSD should consider treating the LPA in the monitoring well (MW-LPA) and then run a brief injection test.

The testing protocol would include the following activities:

- Install and develop LPA monitoring well (MW-LPA).
- Run step drawdown test.
- Treat LPA with an aluminum chloride flush
- Run step drawdown test
- Inject drinking quality water into the LPA through MW-LPA while monitoring injectivity

Salt flushes can alter the specific capacity of a MAR well, so step drawdown tests are necessary to document the baseline specific capacity, before injecting water. An injection test that injects water several aquifer volumes (3 to 5) beyond the conditioned zone should prove sufficient to determine the effectiveness of the aluminum chloride treatment. A successful test would involve observing no measurable loss in injectivity after starting MAR testing. A local source of potable water can serve as a base for the treatment solution and recharge for the test.

A pilot treatment event using 0.1 molar AlCl_3 was conducted in MW-LPA during October 2017. During the treatment event, HRSD successfully conditioned an aquifer volume extending 20 feet from the well. In a post-treatment step drawdown test, the pumping specific capacity at MW-LPA improved by 20 percent over four stepped-pumping rates. More important, the hydraulic characteristics of MW-LPA remained stable during a 7-day injection test conducted after the treatment. If the treatment had proven a failure, the injection capacity of MW-LPA would have declined precipitously within several hours of starting the test. Moreover, the volume of recharge water during the injection test far exceeded the volume needed to fill a 20-foot radius of the LPA. Thus, potable water migrated outside the treated zone around MW-LPA.

6.4 Next Steps

The next steps involve development of a Recharge Implementation and Operational Plan. This plan will present further refinement of the mitigation approaches with respect to water quality targets (additive types and dosages). The plan will also detail the methods involved in conducting the mitigation strategies addressing the specific mechanics involved in conditioning the aquifer.

References

- Brown, D. L., and Silvey, W.D., Artificial Recharge to a Freshwater-Sensitive Brackish Water Sand Aquifer, Norfolk, Virginia, United States Geological Survey Professional Paper 939, Washington, D.C. 1977
- Breeuwsma, A., de Vries, W., Schoumans, O.F., Kragt, J.F., Use of Models and Soil Survey Information in Assessing Regional Water Quality, Netherlands Soil Survey Institute, Wageningen, the Netherlands, 1986.
- Civan, F., Reservoir Formation Damage; Fundamentals, Modeling, Assessment, and Mitigation, Elsevier Publishing, Houston, TX, 2000.
- Davies, C.W. Ion Association, Butterworths, Washington, D.C., 1962.
- Debye, P., and E. Hückel, E. (1923). "Zur Theorie der Elektrolyte. I. Gefrierpunktserniedrigung und verwandte Erscheinungen" [The theory of electrolytes. I. Lowering of freezing point and related phenomena]. Physikalische Zeitschrift Vol, 24, 1923.
- Drever, J.I., The Geochemistry of Natural Water: Surface and Groundwater Environments. Prentice-Hall, Inc., Upper Saddle River, New Jersey, 1982.
- Dzombak, D.A. and F.M.M. Morel, Surface Complexation Modeling: Hydrous Ferric Oxide. John Wiley and Sons, New York, New York, 1990.
- Evangelou, V.P., Pyrite Oxidation and Its Control, CRC Press, Boca Raton, Florida, 1995 Folk, R.L., Petrology of Sedimentary Rocks, Hemphill Publishing, New York, New York, 1965.
- Gray, D.H., and R.W., Rex, Formation Damage in Sandstones Caused by Clay Damage and Migration, Proceedings of 14th National Conference on Clays and Clay Minerals, Pergamon Press, London, 1966.
- Hem, J. D., Study and Interpretation of the Chemical Characteristics of Natural Water, United States Geological Survey Water-Supply Paper 2254, Alexandria, Virginia, 1986.
- Hewitt, C.H., Analytical Techniques for Recognizing Water-Sensitive Reservoir Rocks, Society of Professional Engineers, Denver, Colorado, 1963
- Heywood, C.E. and Pope, J.P., Simulation of Groundwater Flow in the Coastal Plain Aquifer System of Virginia, United States Geological Survey, Scientific Investigations Report 2009-5039, Reston, Virginia, 2009.
- Honig, E.P., and Mul, P.M., Tables and Equations of the Diffuse Double Layer Repulsion at Constant Potential and Constant Charge, Materials Resource Bulletin, Vol. 6, Elsevier Publishing, Amsterdam, the Netherlands, 1971.
- Jones, G.W., and Pichler, T., Relationship between pyrite stability and arsenic mobility during aquifer storage and recovery in southwest, central Florida, Environmental Science and Technology, Vol. 41, New York, NY, 2007.
- Jurgens, B.C., McMahon, P.B., Chapelle, F.H., and Eberts, S.M., An Excel Workbook for Identifying Redox Processes in Ground Water, U.S. Geological Survey Open-File Report 2009-1004, Denver, Colorado, 2009.
- Khilar, K.C. and Fogler, H.S., Mathematical Models for Permeability Reductions Due to Migration of Fines, in Migration of Fines in Porous Media, Springer, New York, New York, 1984.
- Khilar, K.C. and Fogler, H.S., Reduction of Water Sensitivity in Sandstone, in Surface Phenomena In Enhanced Oil Recovery, Springer, New York, New York, 1984.

- Konikow, L.F., August, L.L., and Voss, C.I., *Effects of Clay Dispersion on Aquifer Storage and Recovery in Coastal Aquifers, Transport in Porous Media*, Vol. 43, Springer International Publishing, New York, New York, 2001.
- Langmuir, D., *Aqueous Environmental Geochemistry*, Prentice-Hall, Inc., Upper Saddle River, New Jersey, 1997.
- Kolker, A., and Nordstrom, D.K., *Occurrence and microdistribution of arsenic in pyrite*, United States Geological Survey Workshop – Arsenic in the Environment, Denver, Colorado, 2009.
- McFarland, E.R., and Bruce, T.S., *The Virginian Coastal Plain Hydrogeologic Framework*, United States Geological Survey Professional Paper 1731, Reston, Virginia, 2006.
- Meade, R.H., *Removal of Water and Rearrangement of Particles During Compaction of Clayey Sediments-Review*, *Mechanics of Aquifer Systems*, United Survey Professional Paper, 497-B, Washington, D.C., 1964.
- Meng, A.A., and Harsh, J.F., *Hydrogeologic Framework of the Virginia Coastal Plain*, United States Geological Survey Professional Paper 1404-C, Washington, D.C. 1988.
- Postma, D., *Pyrite and Siderite Formation in Brackish and Freshwater Swamp Sediments*, *American Journal of Science*, V 282, P. 1151-1183, New York, New York, 1982.
- Parkhurst, D.L., *Users Guide to PHREEQC – A Computer Program for Speciation, Reaction-Path, Advective-Transport, Inverse Geochemical Calculations*, U.S. Geological Survey Water Resources Investigation Report 95-4227, Lakewood, Colorado, 1996.
- Pyne, D.G., *Aquifer Storage and Recovery: A Guide to Groundwater Recharge Through Wells*. ASR Press: Gainesville, Florida, 2005.
- Reed, M.G., *Stabilization of Formation Clays with Hydroxy-Aluminum Solutions*, *Journal of Petroleum Technology*, July 1972, 860 to 864, Denver, Colorado.
- Stuyfzand, P.J., *Hydrochemistry and Hydrology of the Coastal Dune area of the Western Netherlands*, KIWA, Nieuwegein, The Netherlands, 1993.
- Stuyfzand, P.J., Putters, B., *Hydrogeochemical patterns, processes and mass transfers during aquifer storage and recovery (ASR) in an anoxic, sandy aquifer*, *Applied Geochemistry*, Elsevier, Vol. 27, Amsterdam, the Netherlands, 2012.
- Stuyfzand, P.J., Antoniou, E.A., and van Breukelen, B.M., *Reactive transport modeling of an aquifer storage and recovery (ASR) pilot to assess long-term water quality improvement and potential solutions*, *Applied Geochemistry*, Vol. 28 Elsevier, Amsterdam, the Netherlands, 2013.
- Treifke, R.H., *Geologic Studies Coastal Plain of Virginia*, Bulletin 83, Virginia Division of Mineral Resources, Richmond, Virginia, 1973.
- Truesdell, A.H. and Jones, B.F., *WATEQ, A Computer Program for Calculating Chemical Equilibrium of Natural Waters*, U.S. Geological Survey Journal of Research 2, 1974.
- Virginia Department of Environmental Quality, *Virginia Coastal Plain Model 2005 Withdrawals Simulation*, Richmond, Virginia, 2006.
- Warner, D.L., and Lehr, J.H., *Subsurface Wastewater Injection*, Premier Press, Berkeley, California.